

Doctoral Thesis

**Development of the Magnetic-Field-Containing
Relativistic Tight-Binding Approximation Method:
Revisiting the de Haas-van Alphen Effect**

〔磁場を含んだ相対論的強束縛近似法の開発：ド・ハ
ースーファン・アルフェン効果の再考〕



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September, 2015

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Dedication

This thesis is dedicated to my most respectable and beloved father the late Tikeshwor Hamal and my mother the late Sharashwati Hamal.

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Chapter 1

Introduction

Silicon is the most common semiconductor material, and is known to be the most pure and ideal crystal that the human being is able to handle. In today's industry, the silicon crystal is one of the most momentous materials used as substrates of semiconductor devices.

Recently, the softening in elastic constants of silicon is observed in low temperature ultrasonic experiments [1]. This phenomenon has attracted much attention because the density of the vacancies in silicon can be evaluated from the behavior of elastic softening [1]. Several authors have studied this phenomenon theoretically by using a kind of model that includes the adjustable or phenomenological parameters in the Hamiltonian [2-7]. It is pointed out that both the Zeeman effect and spin-orbit interaction, which is one of the relativistic effects, play an important role on the suppression of the elastic softening. The negative (unusual) value of the coupling constant of the spin-orbit interaction is used in their works [2,7] in order to explain the above phenomena. However its validity remains to be proven. If a calculation method of relativistic energy bands for materials immersed in the uniform magnetic field is developed, then it will become a reliable method not only to check the validity of the arguments based on the model Hamiltonian [2-6], but also to investigate the above phenomenon in a first principles way. So, we need a first principle calculation method that can describe the effects of both relativity and magnetic field, as the first step toward clarifying the above mentioned phenomenon.

It is generally difficult to incorporate the magnetic field and relativistic effects simultaneously into the calculation method of the electronic structure. Insofar, as the non-relativistic method goes, the tight-binding (TB) approximation method has been developed and applied to some systems [8-10]. In these non-relativistic TB methods, the Peierls substitution [11,12] or the Peierls phase [9,13] is utilized to construct the effective Hamiltonian for Bloch electrons in the uniform magnetic field. Calculation methods other than the TB approximation method have also been presented, though the relativistic effects are not taken into

account in these methods. For example, Zak proposed a method to use the so-called kq functions as basis functions in calculating matrix elements of the Hamiltonian [14-17]. Actual calculations using kq functions are performed in several papers [18-21]. However, their applications are limited to simple model systems. Namely, it is not easy to apply the kq functions method to realistic crystalline materials immersed in the magnetic field.

Of course, there exist a lot of relativistic calculation methods of electronic structures for the zero magnetic field case. For instance, the relativistic linear augmented-plane-wave (RLAPW) method [22-24] has been developed and applied successfully to f -electron materials [25-28]. Thus the electronic structure calculation method that can deal with magnetic field and relativistic effects simultaneously have not yet been developed so far.

In this study, the relativistic TB approximation method is newly developed. This new method is applicable to actual materials immersed in the uniform magnetic field. This is hereafter referred to as the magnetic-field-containing relativistic tight-binding approximation method (MFRTB method). In the MFRTB method, both magnetic field and relativistic effects are taken into consideration by treating the Dirac equation for an electron that moves in both uniform magnetic field and periodic potential of a crystal.

As mentioned above, the development of the MFRTB method is the first thing to be done for the purpose of revealing the mechanism of the elastic softening and its suppression observed in the boron-doped silicon. In addition to the above application, the MFRTB method may have another interesting applications, because this method may become a useful first-principles calculation method that enables us to describe the physical phenomena observed in a magnetic field. In this study, we use the MFRTB method to describe the de Haas-van Alphen effect (dHvA effect) [29-31]. In what follows, I explain the reason why the dHvA effect is an interesting target of the MFRTB method.

The dHvA effect [29-31] is an oscillatory behavior of the magnetization as a function of magnetic field. Measurement of the dHvA effect are widely used to probe the geometry of Fermi surface, the cyclotron effective mass and the scattering lifetime of the conduction electrons [32]. The magnetic oscillation was first discussed by Landau [33] independently of the experiments by de Haas and van Alphen. In the formulation by Landau, the oscillatory behavior of the magnetization is described by means of quantized energy levels (Landau levels) that are obtained by solving the Schrödinger equation for a free electron in the uniform magnetic field [33]. However the formula cannot explain the dependence of the magnetic oscillation on the direction of magnetic field that is experimentally observed [34]. This is due to an oversimplified argument such that the characteristics of individual metals are not taken into consideration [34].

More realistic theory of dHvA effect was developed by Onsager in 1952 [35] as well as by Lifshitz and Kosevich in 1956 [36]. The latter is called Lifshitz-Kosevich (LK) formula and is recognized as the standard theory for the dHvA effect [32, 34]. The LK formula is based on the assumption that the orbital motion of electron is quantized even when the magnetic field is applied to the crystalline solids. This quantization is derived by using both the Bohr-Sommerfeld quantization rule and the semi-classical equation of motion for the Bloch electron in the presence of uniform magnetic field [32, 34-36]. Corresponding to the orbital quantization, the energy levels of the electrons are also quantized. In LK formulation, the dHvA effect is explained from such quantized energy levels. When the quantized energy levels cross the Fermi surface by increasing the magnetic field, every time one energy level matches with the Fermi energy, one oscillation of the magnetization is produced [32, 34-36]. The LK formula is commonly used in estimating the extremal cross-section of the Fermi

surface, cyclotron effective mass and scattering lifetime of electrons from the experimental data of the dHvA effect [25, 26].

As mentioned above, in the LK formula the Bohr-Sommerfeld quantization rule and the semi-classical equation of motion of Bloch electron in the presence of magnetic field are used to achieve the quantized energy levels of the electron [32, 34-36]. On the one hand, of course, it would be desirable to get the quantized energy levels of the electron by solving the Schrödinger equation or Dirac equation for an electron in both periodic potential and uniform magnetic field [34, 37]. However, unfortunately, it has been difficult to solve them directly [4, 37]. Since the MFRTB method is the first principle calculation method that is applicable to calculate the electronic structures of various kinds of realistic materials immersed in the uniform magnetic field [38], the MFRTB method is expected to describe the dHvA effect from the viewpoint of the first-principles calculation. This is the reason why the alternative expression of the dHvA effect is an interesting application of our MFRTB method.

In this work, the MFRTB method is applied to the simple cubic lattice immersed in the uniform magnetic field. It is shown that the dHvA effect can successfully be revisited by means of MFRTB method. Also, we discuss the validity of LK formula by comparing the period of the magnetic oscillation obtained by the MFRTB method with that calculated on the basis of LK formula. Furthermore, it is shown that additional oscillation peaks, which cannot be predicted by the LK formula, appear in the magnetization.

This thesis is organized as follows. In Chapter 2, the relativistic TB method for zero magnetic field case is described as the preliminary discussion of the MFRTB method. The relativistic version of the Slater-Koster table, which is used in calculating the relativistic hopping integrals for the zero magnetic field case, is presented in this chapter. Next, the formulation of the MFRTB method is presented in Chapter 3. It is shown that the magnetic hopping integrals are approximately expressed in terms of both relativistic hopping integrals for zero magnetic field case and magnetic-field dependent phase factor. The application of the MFRTB method to the two dimensional square lattice is discussed in Chapter 4. By comparing the present results with the Hofstadter's one, the validity and advantages of the MFRTB method is presented in this chapter. The application of the MFRTB method to a real material is described in Chapter 5. The electronic structure of the crystalline silicon immersed in a uniform magnetic field is revealed by means of the MFRTB method. Dependences of energy spectra both on the magnitude of the magnetic field and on the wave vector are discussed in this chapter. In Chapter 6, the MFRTB method is applied to a simple cubic lattice immersed in a uniform magnetic field, in order to show that the dHvA effect can be revisited by means of MFRTB method. The validity of the LK formula and additional peaks that are not predicted by the LK formula are also discussed in this chapter. Finally, the concluding remarks of this thesis are given in Chapter 7.

Chapter 2

Relativistic TB approximation method for zero magnetic field

2.1 Matrix elements of Hamiltonian

The Dirac equation for an electron in periodic potential is given by [39]

$$H\Psi_{\alpha,k}(\mathbf{r}) = E_{\alpha,k}\Psi_{\alpha,k}(\mathbf{r}) \quad (2.1)$$

With

$$H = c\boldsymbol{\alpha} \cdot \mathbf{p} + \beta mc^2 + \sum_{\mathbf{R}_n} \sum_i V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i), \quad (2.2)$$

where m and c denote the rest mass of electron and velocity of light respectively. Similarly $\boldsymbol{\alpha} = (\alpha_x, \alpha_y, \alpha_z)$ and β stand for the usual 4×4 matrices [39]. In Eq. (2.2) $V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i)$ is the scalar potential caused by the nucleus of an atom a_i located at $\mathbf{R}_n + \mathbf{d}_i$, where \mathbf{R}_n and \mathbf{d}_i denote the translation vector of the lattice and the vector specifying position of the atom a_i , respectively. The subscripts α and \mathbf{k} of the four component eigen function $\Psi_{\alpha,k}(\mathbf{r})$ denote the band index and crystal momentum, respectively.

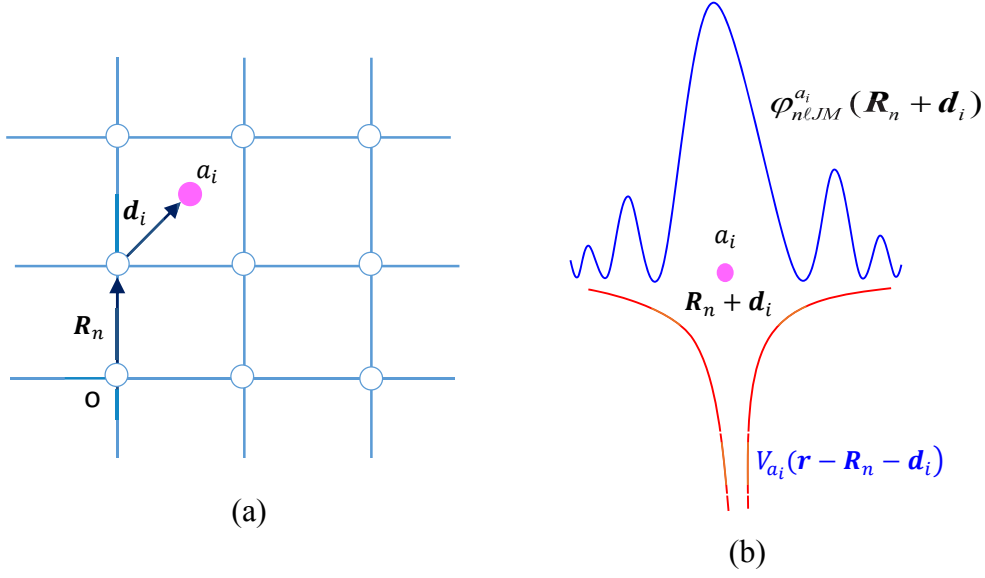


Fig. 2.1 (a) Crystal structure and (b) Relativistic atomic orbital $\varphi_{n\ell JM}^{a_i}(\mathbf{R}_n + \mathbf{d}_i)$ of an atom a_i .

Similarly to the non-relativistic tight-binding (TB) approximation method, $\Psi_{\alpha,k}(\mathbf{r})$ is expanded by using the Bloch sum of the relativistic atomic orbitals as the basis functions. We have

$$\Psi_{\alpha,k}(\mathbf{r}) = \sum_{n\ell JM} \sum_i b_{n\ell JM,i}^{\alpha,k} B_{n\ell JM}^{a_i,k}(\mathbf{r}), \quad (2.3)$$

where $b_{n\ell JM,i}^{\alpha,k}$ is the expansion coefficient, and $B_{n\ell JM}^{a_i,k}(\mathbf{r})$ denotes the Bloch sum which is given by

$$B_{n\ell JM}^{a_i,k}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum e^{ik \cdot (\mathbf{R}_n + \mathbf{d}_i)} \varphi_{n\ell JM}^{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i), \quad (2.4)$$

where $\varphi_{n\ell JM}^{a_i}(\mathbf{r})$ is the relativistic atomic orbital of an atom a_i . In Eqs. (2.3) and (2.4), n , ℓ , J and M are the principal, azimuthal, total angular momentum and magnetic quantum numbers, respectively. The number ℓ is related to parity, which is conserved in the atomic system [39]. The relativistic atomic orbital obeys the following Dirac equation

$$[\mathbf{c}\boldsymbol{\alpha} \cdot \mathbf{p} + \beta mc^2 + V_{a_i}(\mathbf{r})] \varphi_{n\ell JM}^{a_i}(\mathbf{r}) = \bar{\epsilon}_{n\ell JM}^{a_i} \varphi_{n\ell JM}^{a_i}(\mathbf{r}), \quad (2.5)$$

where $\bar{\varepsilon}_{n\ell JM}^{a_i}$ denotes the atomic spectrum for zero magnetic field. It should be noted that $\varphi_{n\ell JM}^{a_i}(\mathbf{r})$ is generally written by

$$\varphi_{n\ell JM}^{a_i}(\mathbf{r}) = \frac{1}{r} \begin{bmatrix} F_{n\ell J}^{a_i}(\mathbf{r}) y_{\ell,J}^M(\theta, \phi) \\ iG_{n\ell J}^{a_i}(\mathbf{r}) y_{2J-\ell,J}^M(\theta, \phi) \end{bmatrix}, \quad (2.6)$$

where $F_{n\ell J}^{a_i}(\mathbf{r})$ and $G_{n\ell J}^{a_i}(\mathbf{r})$ denote the large and small components of the radial part of $\varphi_{n\ell JM}^{a_i}(\mathbf{r})$ respectively. Similarly, $y_{\ell,J}^M(\theta, \phi)$ is the spinor spherical harmonics [39]. From Eqs. (2.1), (2.3) and (2.4), we have

$$H \sum_{n\ell JM} \sum_i \sum_{\mathbf{R}_n} b_{n\ell JM,i}^{\alpha,k}(\mathbf{r}) e^{i\mathbf{k}\cdot(\mathbf{R}_n+\mathbf{d}_i)} \varphi_{n\ell JM}^{a_i}(\mathbf{r}-\mathbf{R}_n-\mathbf{d}_i) = E_k \sum_{n\ell JM} \sum_i \sum_{\mathbf{R}_n} b_{n\ell JM,i}^{\alpha,k}(\mathbf{r}) e^{i\mathbf{k}\cdot(\mathbf{R}_n+\mathbf{d}_i)} \varphi_{n\ell JM}^{a_i}(\mathbf{r}-\mathbf{R}_n-\mathbf{d}_i). \quad (2.7)$$

Multiplying on both side of Eq. (2.7), by $\varphi_{n'\ell'JM'}^{a_j}(\mathbf{r}-\mathbf{d}_j)^\dagger$ and integrating it, we get

$$\begin{aligned} \sum_{n\ell JM} \sum_i \sum_{\mathbf{R}_n} b_{n\ell JM,i}^{\alpha,k}(\mathbf{r}) e^{i\mathbf{k}\cdot(\mathbf{R}_n+\mathbf{d}_i)} \int \varphi_{n'\ell'JM'}^{a_j}(\mathbf{r}-\mathbf{d}_j)^\dagger H \varphi_{n\ell JM}^{a_i}(\mathbf{r}-\mathbf{R}_n-\mathbf{d}_i) d^3r = E_k \sum_{n\ell JM} \sum_i \sum_{\mathbf{R}_n} b_{n\ell JM,i}^{\alpha,k}(\mathbf{r}) \\ \times e^{i\mathbf{k}\cdot(\mathbf{R}_n+\mathbf{d}_i)} \int \varphi_{n'\ell'JM'}^{a_j}(\mathbf{r}-\mathbf{d}_j)^\dagger \varphi_{n\ell JM}^{a_i}(\mathbf{r}-\mathbf{R}_n-\mathbf{d}_i) d^3r \end{aligned} \quad (2.8)$$

Let us define the relativistic hopping integrals as

$$t_{n'\ell'JM',n\ell JM}^{a_j a_i}(\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j) = \int \varphi_{n'\ell'JM'}^{a_j}(\mathbf{r}-\mathbf{d}_j)^\dagger H \varphi_{n\ell JM}^{a_i}(\mathbf{r}-\mathbf{R}_n-\mathbf{d}_i) d^3r. \quad (2.9)$$

We assume that $\varphi_{n\ell JM}^{a_i}(\mathbf{r}-\mathbf{R}_n-\mathbf{d}_i)$ is sufficiently localized around $\mathbf{R}_n + \mathbf{d}_i$ so that it satisfies

$$\int \varphi_{n\ell JM}^{a_i}(\mathbf{r}-\mathbf{R}_n-\mathbf{d}_i)^\dagger \varphi_{n'\ell'JM'}^{a_j}(\mathbf{r}-\mathbf{R}_m-\mathbf{d}_j) d^3r \approx \delta_{\mathbf{R}_n+\mathbf{d}_i, \mathbf{R}_m+\mathbf{d}_j} \delta_{n\ell JM, n'\ell'JM'}. \quad (2.10)$$

By using Eqs. (2.9) and (2.10), Eq. (2.8), becomes

$$\sum_{n\ell JM} \sum_i \left\{ \sum_{\mathbf{R}_n} e^{i\mathbf{k}\cdot(\mathbf{R}_n+\mathbf{d}_i)} t_{n'\ell'JM',n\ell JM}^{a_j a_i}(\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j) \right\} b_{n\ell JM,i}^{\alpha,k} \approx E_{\mathbf{k}} \sum_{n\ell JM} \sum_i b_{n\ell JM,i}^{\alpha,k} \sum_{\mathbf{R}_n} e^{i\mathbf{k}\cdot(\mathbf{R}_n+\mathbf{d}_i)} \delta_{n'\ell'JM',n\ell JM} \delta_{\mathbf{R}_n+\mathbf{d}_i,\mathbf{d}_j}. \quad (2.11)$$

Rearranging Eq. (2.11), we have

$$\sum_{n\ell JM} \sum_i \left\{ \sum_{\mathbf{R}_n} e^{i\mathbf{k}\cdot(\mathbf{R}_n+\mathbf{d}_i-\mathbf{d}_j)} t_{n'\ell'JM',n\ell JM}^{a_j a_i}(\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j) - E_{\mathbf{k}} \delta_{n'\ell'JM',n\ell JM} \delta_{i,j} \right\} b_{n\ell JM,i}^{\alpha,k} \approx 0. \quad (2.12)$$

Let us define the matrix element of Hamiltonian by

$$H_{(n'\ell'JM')_j,(n\ell JM)_i}(\mathbf{k}) = \sum_{\mathbf{R}_n} e^{i\mathbf{k}\cdot(\mathbf{R}_n+\mathbf{d}_i-\mathbf{d}_j)} t_{n'\ell'JM',n\ell JM}^{a_j a_i}(\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j). \quad (2.13)$$

Then finally, Eq. (2.12) becomes

$$\sum_{n\ell JM} \sum_i H_{(n'\ell'JM')_j,(n\ell JM)_i}(\mathbf{k}) b_{n\ell JM,i}^{\alpha,k} \approx E_{\mathbf{k}} \delta_{n'\ell'JM',n\ell JM} \delta_{i,j} b_{n\ell JM,i}^{\alpha,k}. \quad (2.14)$$

It should be noted that the matrix element of Hamiltonian defined in Eq. (2.13) is hermite. This fact can be shown in Appendix A by using the property of the relativistic hopping integral that will be discussed in Sec. 2.2.3.

By solving Eq. (2.14), we can get the eigenvalues $E_{\mathbf{k}}$ and eigen functions $\Psi_{\alpha,\mathbf{k}}(\mathbf{r})$ via Eq. (2.3) for each \mathbf{k} . In order to solve Eq. (2.14), we need to calculate the hopping integral $t_{n'\ell'JM',n\ell JM}^{a_j a_i}(\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j)$. In the subsequent sections, I explain how to calculate $t_{n'\ell'JM',n\ell JM}^{a_j a_i}(\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j)$.

2.2 Relativistic hopping integrals

Let us calculate the relativistic hopping integral $t_{n'\ell'JM',n\ell JM}^{a_j a_i}(\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j)$ in the following conditions:

- i. $\mathbf{R}_n = 0$ and $\mathbf{d}_i = \mathbf{d}_j$
- ii. $\mathbf{R}_n \neq 0$ or $\mathbf{d}_i \neq \mathbf{d}_j$

2.2.1 Relativistic hopping integral in the case of $R_n = 0$ and $d_i = d_j$:

In this case, Eq. (2.9) becomes

$$\begin{aligned}
t_{n'\ell'JM',n\ell JM}^{a_j a_i}(\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j) &= \int \varphi_{n'\ell'JM'}^{a_j}(\mathbf{r} - \mathbf{d}_j)^\dagger \{c\boldsymbol{\alpha} \cdot \mathbf{P} + \beta mc^2 + \sum_{\mathbf{R}_m} \sum_j V_{a_i}(\mathbf{r} - \mathbf{R}_m - \mathbf{d}_j)\} \varphi_{n\ell JM}^{a_i}(\mathbf{r} - \mathbf{d}_i) d^3 r \\
&= \int \varphi_{n'\ell'JM'}^{a_j}(\mathbf{r} - \mathbf{d}_j)^\dagger \{c\boldsymbol{\alpha} \cdot \mathbf{P} + \beta mc^2 + V_{a_i}(\mathbf{r} - \mathbf{d}_i)\} \varphi_{n\ell JM}^{a_i}(\mathbf{r} - \mathbf{d}_i) d^3 r + \\
&\quad \int \varphi_{n'\ell'JM'}^{a_j}(\mathbf{r} - \mathbf{d}_j)^\dagger \left\{ \sum_{\substack{\mathbf{R}_m \neq 0 \\ i' \neq i}} \sum_{a_i} V_{a_i}(\mathbf{r} - \mathbf{R}_m - \mathbf{d}_i) \right\} \varphi_{n\ell JM}^{a_i}(\mathbf{r} - \mathbf{d}_i) d^3 r.
\end{aligned}$$

Substituting Eq. (2.5) in the first line of above equation, we have

$$\begin{aligned}
t_{n'\ell'JM',n\ell JM}^{a_j a_i}(\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j) &= \bar{\varepsilon}_{n\ell J}^{a_i} \delta_{n'\ell'JM',n\ell JM} \delta_{j,i} + \int \varphi_{n'\ell'JM'}^{a_j}(\mathbf{r} - \mathbf{d}_i)^\dagger \left\{ \sum_{\substack{\mathbf{R}_m \\ (\mathbf{R}_m + \mathbf{d}_k \neq \mathbf{d}_i)}} \sum_k V_{a_k}(\mathbf{r} - \mathbf{R}_m - \mathbf{d}_k) \right\} \\
&\quad \times \varphi_{n\ell JM}^{a_i}(\mathbf{r} - \mathbf{d}_i) d^3 r \tag{2.15}
\end{aligned}$$

This second term of Eq. (2.15) denotes the energy of the crystal field. Since the relativistic atomic orbitals $\varphi_{n'\ell'JM'}^{a_j}(\mathbf{r} - \mathbf{d}_i)$ and $\varphi_{n\ell JM}^{a_i}(\mathbf{r} - \mathbf{d}_i)$ are localized around $\mathbf{r} = \mathbf{d}_i$, we can reasonably approximate $V_{a_k}(\mathbf{r} - \mathbf{R}_m - \mathbf{d}_k)$ by the constant value at $\mathbf{r} = \mathbf{d}_i$ in the integral. Due to the orthogonality of $\varphi_{n'\ell'JM'}^{a_j}(\mathbf{r} - \mathbf{d}_i)$ and $\varphi_{n\ell JM}^{a_i}(\mathbf{r} - \mathbf{d}_i)$ for $(n', \ell', J', M') \neq (n, \ell, J, M)$, the above integral vanishes under this approximation. Therefore, the energy of the crystal field is reasonably approximated by

$$\int \varphi_{n'\ell'JM'}^{a_j}(\mathbf{r} - \mathbf{d}_i)^\dagger \left\{ \sum_{\substack{\mathbf{R}_m \\ (\mathbf{R}_m + \mathbf{d}_k \neq \mathbf{d}_i)}} \sum_k V_{a_k}(\mathbf{r} - \mathbf{R}_m - \mathbf{d}_k) \right\} \varphi_{n\ell JM}^{a_i}(\mathbf{r} - \mathbf{d}_i) d^3 r \approx \delta_{n'\ell'JM',n\ell JM} \Delta \bar{\varepsilon}_{n\ell J}^{a_i} \tag{2.16}$$

with

$$\Delta \bar{\varepsilon}_{n\ell J}^{a_i} = \int \varphi_{n\ell JM}^{a_i}(\mathbf{r} - \mathbf{d}_i)^\dagger \left\{ \sum_{\substack{\mathbf{R}_m \\ (\mathbf{R}_m + \mathbf{d}_k \neq \mathbf{d}_i)}} \sum_k V_{a_k}(\mathbf{r} - \mathbf{R}_m - \mathbf{d}_k) \right\} \varphi_{n\ell JM}^{a_i}(\mathbf{r} - \mathbf{d}_i) d^3 r. \tag{2.17}$$

Substituting Eq. (2.17) into Eq. (2.15) leads to

$$t_{n'\ell'JM',n\ell JM}^{a_j a_i}(\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j) = (\bar{\mathcal{E}}_{n\ell J}^{a_i} + \Delta \bar{\mathcal{E}}_{n\ell JM}^{a_i}) \delta_{n'\ell'JM',n\ell JM} \delta_{j,i}. \quad (2.18)$$

2.2.2 Relativistic hopping integral in the case of $R_n \neq 0$ or $d_i \neq d_j$:

In this case, Eq. (2.9) becomes

$$\begin{aligned} & t_{n'\ell'JM',n\ell JM}^{a_j a_i}(\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j) \\ &= \int \varphi_{n'\ell'JM'}^{a_j}(\mathbf{r} - \mathbf{d}_j)^\dagger \left\{ \{c\boldsymbol{\alpha} \cdot \mathbf{P} + \beta mc^2 + \frac{V_{a_j}(\mathbf{r} - \mathbf{d}_j) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i)}{2}\} + \frac{V_{a_j}(\mathbf{r} - \mathbf{d}_j) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i)}{2} \right. \\ & \quad \left. + \sum_{\substack{\mathbf{R}_{n'} \\ (\mathbf{R}_{n'} \neq 0) \\ (\mathbf{R}_{n'} \neq \mathbf{R}_n)}} \sum_{\substack{i,i' \\ i' \neq 0 \\ i \neq i'}} V_{a_i}(\mathbf{r} - \mathbf{R}_{n'} - \mathbf{d}_{i'}) \right\} \varphi_{n\ell JM}^{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i) d^3 r \\ &= \frac{1}{2} \int \varphi_{n'\ell'JM'}^{a_j}(\mathbf{r} - \mathbf{d}_j)^\dagger \{c\boldsymbol{\alpha} \cdot \mathbf{P} + \beta mc^2 + V_{a_j}(\mathbf{r} - \mathbf{d}_j)\} \varphi_{n\ell JM}^{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i) d^3 r + \frac{1}{2} \int \varphi_{n'\ell'JM'}^{a_j}(\mathbf{r} - \mathbf{d}_j)^\dagger \\ & \quad \times \{c\boldsymbol{\alpha} \cdot \mathbf{P} + \beta mc^2 + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i)\} \varphi_{n\ell JM}^{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i) d^3 r + \int \varphi_{n'\ell'JM'}^{a_j}(\mathbf{r} - \mathbf{d}_j)^\dagger \left\{ \frac{V_{a_j}(\mathbf{r} - \mathbf{d}_j)}{2} + \right. \\ & \quad \left. \frac{V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i)}{2} \right\} \varphi_{n\ell JM}^{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i) d^3 r + \sum_{\substack{\mathbf{R}_{n'} \\ (\mathbf{R}_{n'} \neq 0) \\ (\mathbf{R}_{n'} \neq \mathbf{R}_n)}} \sum_{\substack{j,i' \\ i' \neq j \\ i \neq i'}} \int \varphi_{n'\ell'JM'}^{a_j}(\mathbf{r} - \mathbf{d}_j)^\dagger V_{a_i}(\mathbf{r} - \mathbf{R}_{n'} - \mathbf{d}_{i'}) \\ & \quad \times \varphi_{n\ell JM}^{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i) d^3 r \quad (2.19) \end{aligned}$$

Taking first integral in the right hand side of Eq. (2.19), we have

$$\begin{aligned} & \frac{1}{2} \int \varphi_{n'\ell'JM'}^{a_j}(\mathbf{r} - \mathbf{d}_j)^\dagger \{c\boldsymbol{\alpha} \cdot \mathbf{P} + \beta mc^2 + V_{a_j}(\mathbf{r} - \mathbf{d}_j)\} \varphi_{n\ell JM}^{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i) d^3 r \\ &= \frac{1}{2} \bar{\mathcal{E}}_{n\ell J}^{a_i} \int \varphi_{n'\ell'JM'}^{a_j}(\mathbf{r} - \mathbf{d}_j)^\dagger \varphi_{n\ell JM}^{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i) d^3 r \\ &= 0, \end{aligned}$$

where we use Eq. (2.10). Similarly second integral in the RHS of Eq. (2.19) is also zero due to same reason Eq. (2.10). The fourth integral in the RHS of Eq. (2.19) is the three central

integral. Neglecting this integral because of very small numerical value in comparison to other integrals. Finally the remaining integral is two-center, which is given by

$$t_{n'\ell'JM',n\ell JM}^{a_j a_i}(\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j) = \int \varphi_{n'\ell'JM'}^{a_j}(\mathbf{r} - \mathbf{d}_j)^\dagger \left\{ \frac{V_{a_j}(\mathbf{r} - \mathbf{d}_j) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i)}{2} \right\} \varphi_{n\ell JM}^{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i) d^3 r. \quad (2.20)$$

Changing the variable $\mathbf{r} - \mathbf{d}_j = \mathbf{r}'$ then, we have

$$t_{n'\ell'JM',n\ell JM}^{a_j a_i}(\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j) = \int \varphi_{n'\ell'JM'}^{a_j}(\mathbf{r}')^\dagger \left\{ \frac{V_{a_j}(\mathbf{r}') + V_{a_i}(\mathbf{r}' - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right\} \varphi_{n\ell JM}^{a_i}(\mathbf{r}' - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j) d^3 r'. \quad (2.21)$$

Substituting Eqs. (2.18) and (2.21) into (2.13), we get

$$H_{(n'\ell'JM')_j, (n\ell JM)_i}(\mathbf{k}) = (\bar{\varepsilon}_{n\ell J}^{a_i} + \Delta \bar{\varepsilon}_{n\ell J}^{a_i, \mathbf{d}_i}) \delta_{n'\ell'JM', n\ell JM} \delta_{j,i} + \sum_{\mathbf{R}_n} (1 - \delta_{\mathbf{R}_n, 0} \delta_{j,i}) e^{i\mathbf{k} \cdot (\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j)} \times t_{n'\ell'JM', n\ell JM}^{a_j a_i}(\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j). \quad (2.22)$$

2.3 Properties of relativistic hopping integral and TB parameters

Similarly to the non-relativistic hopping integrals, the relativistic hopping integrals has same important properties. In this section, we summarize the properties. The relativistic hopping integral $t_{n'\ell'JM', n\ell JM}^{a_j a_i}(\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j)$ has the following properties-

$$\text{Property-I} \quad t_{n'\ell'JM', n\ell JM}^{a_j a_i}(\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j) = t_{n\ell JM, n'\ell'JM'}^{a_i a_j} \{-(\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j)\}^* \quad (2.23)$$

$$\text{Property-II} \quad t_{n'\ell'JM', n\ell JM}^{a_j a_i}(\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j) = (-1)^{\ell + \ell'} t_{n'\ell'JM', n\ell JM}^{a_i a_j}(\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j)^* \quad (2.24)$$

Property-I guarantees the hermicity of the Hamiltonian matrix [see, Appendix A] and the property-II will be used later. As shown in the next section (Sec. 2.4), the $t_{n'\ell'JM', n\ell JM}^{a_j a_i}(\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j)$ can be expressed in terms of several relativistic tight-binding parameters, similar to the case of non-relativistic hopping integral [40]. With the reference of

non-relativistic case [40,41], the relativistic TB parameter is defined as the relativistic hopping integral between two sites that are placed on the z -axis. If atoms a_j and a_i are placed at the origin and the distance $|\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j|$ away from the origin, respectively, then the relativistic TB parameter is written as $t_{n'\ell'J'M',n\ell JM}^{a_j a_i}(|\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j| \mathbf{e}_z)$, where \mathbf{e}_z denotes the unit vector in the direction of z -axis. This special type of relativistic hopping integral has the following properties in addition to properties I and II.

$$\text{Property-III} \quad t_{n'\ell'J'M',n\ell JM}^{a_j a_i}(|\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j| \mathbf{e}_z) = t_{n'\ell'J'M',n\ell JM}^{a_j a_i}(|\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j| \mathbf{e}_z) \delta_{M,M'}, \quad (2.25)$$

$$\text{Property-IV} \quad t_{n'\ell'J'-M',n\ell J-M}^{a_j a_i}(|\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j| \mathbf{e}_z) = (-1)^{J+J'+\ell+\ell'+1} t_{n'\ell'J'M',n\ell JM}^{a_j a_i}(|\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j| \mathbf{e}_z). \quad (2.26)$$

Due to properties III and IV, the relativistic TB parameters can be classified by $n, n', \ell, \ell', J, J'$ and $|M|$. If we denote the relativistic TB parameters as

$$\begin{aligned} K_d^{a_j a_i}(n'\ell'J', n\ell J)_{|M|} &= t_{n'\ell'J'M',n\ell JM}^{a_j a_i}(|\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j| \mathbf{e}_z), \\ &= \int \varphi_{n'\ell'J'|M'}^{a_j}(\mathbf{r})^\dagger \left\{ \frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - |\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j| \mathbf{e}_z)}{2} \right\} \varphi_{n\ell JM}^{a_i}(\mathbf{r} - |\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j| \mathbf{e}_z) d^3 r, \end{aligned} \quad (2.27)$$

where the subscript d of $K_d^{a_j a_i}(n'\ell'J', n\ell J)_{|M|}$ is the parameter that shows the dependence of the relativistic TB parameter on $|\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j|$. Specially, if $|\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j|$ is equal to the distance between the nearest neighboring atoms, second nearest neighboring atoms, and so on, then d takes 1, 2, \dots respectively. In the case where ℓ takes the values of 0 and 1, we have ten kinds of relativistic TB parameters, i.e.,

$$\begin{aligned} &K_d^{a_j a_i} \left(n'0\frac{1}{2}, n0\frac{1}{2} \right)_{1/2}, \quad K_d^{a_j a_i} \left(n'0\frac{1}{2}, n1\frac{1}{2} \right)_{1/2}, \quad K_d^{a_j a_i} \left(n'0\frac{1}{2}, n1\frac{3}{2} \right)_{1/2}, \quad K_d^{a_j a_i} \left(n'1\frac{1}{2}, n0\frac{1}{2} \right)_{1/2}, \\ &K_d^{a_j a_i} \left(n'1\frac{1}{2}, n1\frac{1}{2} \right)_{1/2}, \quad K_d^{a_j a_i} \left(n'1\frac{1}{2}, n1\frac{3}{2} \right)_{1/2}, \quad K_d^{a_j a_i} \left(n'1\frac{3}{2}, n0\frac{1}{2} \right)_{1/2}, \quad K_d^{a_j a_i} \left(n'1\frac{3}{2}, n1\frac{1}{2} \right)_{1/2}, \\ &K_d^{a_j a_i} \left(n'1\frac{3}{2}, n1\frac{3}{2} \right)_{1/2}, \quad K_d^{a_j a_i} \left(n'1\frac{3}{2}, n1\frac{3}{2} \right)_{3/2}. \end{aligned}$$

In the case of monoatomic crystals such as crystalline silicon, the relativistic TB parameters

are of course, independent of a_i and a_j . Therefore the relativistic TB parameters can be denoted by $K_d(n'\ell'J', n\ell J)_{|M|}$. Due to the property-II, [Eq. (24)], $K_d(n'\ell'J', n\ell J)_{|M|}$ and $K_d(n\ell J, n'\ell'J')_{|M|}$ are not independent of each other. Therefore we have seven kinds of relativistic TB parameters in this case. i.e.

$$K_d^{a_j a_i} \left(n'0\frac{1}{2}, n0\frac{1}{2} \right)_{1/2}, \quad K_d^{a_j a_i} \left(n'0\frac{1}{2}, n1\frac{1}{2} \right)_{1/2}, \quad K_d^{a_j a_i} \left(n'0\frac{1}{2}, n1\frac{3}{2} \right)_{1/2}, \quad K_d^{a_j a_i} \left(n'1\frac{1}{2}, n1\frac{1}{2} \right)_{1/2},$$

$$K_d^{a_j a_i} \left(n'1\frac{1}{2}, n1\frac{3}{2} \right)_{1/2}, \quad K_d^{a_j a_i} \left(n'1\frac{3}{2}, n1\frac{3}{2} \right)_{1/2}, \quad K_d^{a_j a_i} \left(n'1\frac{3}{2}, n1\frac{3}{2} \right)_{3/2}.$$

In order to express $K_d(n\ell J, n'\ell'J')_{|M|}$ by using the large and small components of the relativistic atomic orbitals, we introduce the following notations:

2.4 Relativistic version of the Slater-koster table

As mentioned before, $t_{n'\ell'JM', n\ell JM}^{a_j a_i}(\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j)$ can be expressed in terms of several relativistic TB parameters $K_d^{a_j a_i}(n'\ell'J', n\ell J)_{|M|}$. This fact is similar to the case of non-relativistic hopping integral. In the case of non-relativistic hopping integrals, Slater and Koster [40] have given a useful table in which the non-relativistic hopping integrals are expressed in the linear combination of several TB parameters. This table is sometimes called Slater-Koster table. In this section, we upgrade the Slater-Koster table to the relativistic version. The spinor spherical harmonic $y_{\ell J}^M(\theta, \phi)$ is

$$y_{\ell J}^M(\theta, \phi) = \begin{cases} \begin{bmatrix} \sqrt{\frac{J+M}{2}} Y_{\ell, M-\frac{1}{2}}(\theta, \phi) \\ \sqrt{\frac{J-M}{2}} Y_{\ell, M+\frac{1}{2}}(\theta, \phi) \end{bmatrix} & \text{for } J = \ell + \frac{1}{2} \\ \begin{bmatrix} -\sqrt{\frac{J-M+1}{2(J+1)}} Y_{\ell, M-\frac{1}{2}}(\theta, \phi) \\ \sqrt{\frac{J+M+1}{2(J+1)}} Y_{\ell, M+\frac{1}{2}}(\theta, \phi) \end{bmatrix} & \text{for } J = \ell - \frac{1}{2} \end{cases} \quad (2.28)$$

where $Y_{\ell, M-\frac{1}{2}}(\theta, \phi)$ and $Y_{\ell, M+\frac{1}{2}}(\theta, \phi)$ are the spherical harmonics. From Eqs. (2.6) and (2.28),

the four component relativistic wave function for $J = \ell + \frac{1}{2}$ is given by

$$\varphi_{n\ell JM}^{a_i}(\mathbf{r}) = \frac{1}{r} \begin{bmatrix} F_{n\ell J}^{a_i} \sqrt{\frac{J+M}{2}} Y_{\ell, M-\frac{1}{2}}(\theta, \phi) \\ F_{n\ell J}^{a_i} \sqrt{\frac{J-M}{2}} Y_{\ell, M+\frac{1}{2}}(\theta, \phi) \\ -iG_{n\ell J}^{a_i} \sqrt{\frac{J-M+1}{2(J+1)}} Y_{2J-\ell, M-\frac{1}{2}}(\theta, \phi) \\ iG_{n\ell J}^{a_i} \sqrt{\frac{J+M+1}{2(J+1)}} Y_{2J-\ell, M+\frac{1}{2}}(\theta, \phi) \end{bmatrix}, \quad (2.29)$$

Similarly, for $J = \ell - \frac{1}{2}$, we have

$$\varphi_{n\ell JM}^{a_i}(\mathbf{r}) = \frac{1}{r} \begin{bmatrix} -F_{n\ell J}^{a_i}(r) \sqrt{\frac{J-M+1}{2(J+1)}} Y_{\ell, M-\frac{1}{2}}(\theta, \phi) \\ F_{n\ell J}^{a_i}(r) \sqrt{\frac{J+M+1}{2(J+1)}} Y_{\ell, M+\frac{1}{2}}(\theta, \phi) \\ iG_{n\ell J}^{a_i}(r) \sqrt{\frac{J+M}{2J}} Y_{\ell-1, M-\frac{1}{2}}(\theta, \phi) \\ iG_{n\ell J}^{a_i}(r) \sqrt{\frac{J-M}{2J}} Y_{\ell-1, M+\frac{1}{2}}(\theta, \phi) \end{bmatrix}. \quad (2.30)$$

Substituting Eq. (2.29) or (2.30) into Eq. (2.21), the relativistic hopping integral can be written. There are four cases, i.e.

- i. $J' = \ell' + \frac{1}{2}$ and $J = \ell + \frac{1}{2}$
- ii. $J' = \ell' + \frac{1}{2}$ and $J = \ell - \frac{1}{2}$
- iii. $J' = \ell' - \frac{1}{2}$ and $J = \ell + \frac{1}{2}$
- iv. $J' = \ell' - \frac{1}{2}$ and $J = \ell - \frac{1}{2}$.

The relativistic hopping integral for the case (i) can be written as

$$\begin{aligned}
& t_{n'\ell'JM',n\ell JM}^{a_j a_i}(\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j) \\
&= \int \sqrt{\frac{J'+M'}{2J'}} \frac{1}{rr_{ijn}} F_{n'\ell'J'}^{a_j}(r) Y_{\ell',M'-\frac{1}{2}}^*(\theta, \phi) \left\{ \frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right\} \sqrt{\frac{J+M}{2J}} F_{n\ell J}^{a_i}(r_{ijn}) Y_{\ell, M-\frac{1}{2}}(\theta_{ijn}, \phi_{ijn}) d^3 r \\
&+ \int \sqrt{\frac{J'-M'}{2J'}} \frac{1}{rr_{ijn}} F_{n'\ell'J'}^{a_j}(r) Y_{\ell',M'+\frac{1}{2}}^*(\theta, \phi) \left\{ \frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right\} \sqrt{\frac{J-M}{2J}} \\
&\quad \times F_{n\ell J}^{a_i}(r_{ijn}) Y_{\ell, M+\frac{1}{2}}(\theta_{ijn}, \phi_{ijn}) d^3 r \\
&+ \int -\sqrt{\frac{J'-M'+1}{2(J'+1)}} \frac{1}{rr_{ijn}} \left\{ iG_{n'\ell'J'}^{a_j}(r) \right\}^* Y_{\ell'+1, M'-\frac{1}{2}}^*(\theta, \phi) \left\{ \frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right\} \\
&\quad \times \left\{ -\sqrt{\frac{J-M+1}{2(J+1)}} iG_{n\ell J}^{a_i}(r_{ijn}) \right\} Y_{\ell+1, M-\frac{1}{2}}(\theta_{ijn}, \phi_{ijn}) d^3 r \\
&+ \int \sqrt{\frac{J'+M'+1}{2(J'+1)}} \frac{1}{rr_{ijn}} \left\{ iG_{n'\ell'J'}^{a_j}(r) \right\}^* Y_{\ell'+1, M'+\frac{1}{2}}^*(\theta, \phi) \left\{ \frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right\} \\
&\quad \times \left\{ \sqrt{\frac{J+M+1}{2(J+1)}} iG_{n\ell J}^{a_i}(r_{ijn}) \right\} Y_{\ell+1, M+\frac{1}{2}}(\theta_{ijn}, \phi_{ijn}) d^3 r \tag{2.31}
\end{aligned}$$

Similarly the relativistic hopping integral for the case (ii) can be written as

$$\begin{aligned}
& t_{n'\ell'JM',n\ell JM}^{a_j a_i}(\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j) \\
&= -\int \sqrt{\frac{J'+M'}{2J'}} \frac{1}{rr_{ijn}} F_{n'\ell'J'}^{a_j}(r) Y_{\ell',M'-\frac{1}{2}}^*(\theta, \phi) \left\{ \frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right\} \sqrt{\frac{J-M+1}{2(J+1)}} \\
&\quad \times F_{n\ell J}^{a_i}(r_{ijn}) Y_{\ell, M-\frac{1}{2}}(\theta_{ijn}, \phi_{ijn}) d^3 r \\
&+ \int \sqrt{\frac{J'-M'}{2J'}} \frac{1}{rr_{ijn}} F_{n'\ell'J'}^{a_j}(r) Y_{\ell',M'+\frac{1}{2}}^*(\theta, \phi) \left\{ \frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right\} \sqrt{\frac{J+M+1}{2(J+1)}}
\end{aligned}$$

$$\begin{aligned}
& \times F_{n\ell J}^{a_i}(r_{ijn}) Y_{\ell, M+\frac{1}{2}}(\theta_{ijn}, \phi_{ijn}) d^3 r \\
& + \int -\sqrt{\frac{J'-M'+1}{2(J'+1)}} \frac{1}{rr_{ijn}} \left\{ iG_{n'\ell'J'}^{a_j}(r) \right\}^* Y_{\ell'+1, M'-\frac{1}{2}}^*(\theta, \phi) \left\{ \frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right\} \left\{ \sqrt{\frac{J+M}{2J}} iG_{n\ell J}^{a_i}(r_{ijn}) \right\} \\
& \quad \times Y_{\ell-1, M-\frac{1}{2}}(\theta_{ijn}, \phi_{ijn}) d^3 r \\
& + \int \sqrt{\frac{J'+M'+1}{2(J'+1)}} \frac{1}{rr_{ijn}} \left\{ iG_{n'\ell'J'}^{a_j}(r) \right\}^* Y_{\ell'+1, M'+\frac{1}{2}}^*(\theta, \phi) \left\{ \frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right\} \\
& \quad \times \left\{ \sqrt{\frac{J-M}{2J}} iG_{n\ell J}^{a_i}(r_{ijn}) \right\} Y_{\ell-1, M+\frac{1}{2}}(\theta_{ijn}, \phi_{ijn}) d^3 r \quad (2.32)
\end{aligned}$$

The relativistic hopping integral for the case (iii) can be written as

$$\begin{aligned}
& t_{n'\ell'JM', n\ell JM}^{a_j a_i}(\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j) \\
& = -\int \sqrt{\frac{J'-M'+1}{2(J'+1)}} \frac{1}{rr_{ijn}} F_{n'\ell'J'}^{a_j}(r) Y_{\ell', M'-\frac{1}{2}}^*(\theta, \phi) \left\{ \frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right\} \sqrt{\frac{J+M}{2J}} \\
& \quad \times F_{n\ell J}^{a_i}(r_{ijn}) Y_{\ell, M-\frac{1}{2}}(\theta_{ijn}, \phi_{ijn}) d^3 r \\
& + \int \sqrt{\frac{J'+M'+1}{2(J'+1)}} \frac{1}{rr_{ijn}} F_{n'\ell'J'}^{a_j}(r) Y_{\ell', M'+\frac{1}{2}}^*(\theta, \phi) \left\{ \frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right\} \sqrt{\frac{J-M}{2J}} \\
& \quad \times F_{n\ell J}^{a_i}(r_{ijn}) Y_{\ell, M+\frac{1}{2}}(\theta_{ijn}, \phi_{ijn}) d^3 r \\
& - \int \sqrt{\frac{J'+M'}{2J'}} \frac{1}{rr_{ijn}} \left\{ iG_{n'\ell'J'}^{a_j}(r) \right\}^* Y_{\ell'-1, M'-\frac{1}{2}}^*(\theta, \phi) \left\{ \frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right\} \\
& \quad \times \left\{ \sqrt{\frac{J-M+1}{2(J+1)}} iG_{n\ell J}^{a_i}(r_{ijn}) \right\} Y_{\ell, M-\frac{1}{2}}(\theta_{ijn}, \phi_{ijn}) d^3 r \\
& + \int \sqrt{\frac{J'-M'}{2J'}} \frac{1}{rr_{ijn}} \left\{ iG_{n'\ell'J'}^{a_j}(r) \right\}^* Y_{\ell'-1, M'+\frac{1}{2}}^*(\theta, \phi) \left\{ \frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right\}
\end{aligned}$$

$$\times \left\{ \sqrt{\frac{J+M+1}{2(J+1)}} iG_{n\ell J}^{a_i}(r_{ijn}) \right\} Y_{\ell, M+\frac{1}{2}}(\theta_{ijn}, \phi_{ijn}) d^3 r \quad (2.33)$$

Finally, the relativistic hopping integrals for the case (iv) can be written as

$$\begin{aligned} t_{n'\ell'JM', n\ell JM}^{a_j a_i}(\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j) = & \\ & \int \sqrt{\frac{J'-M'+1}{2(J'+1)}} \frac{1}{rr_{ijn}} F_{n'\ell'J'}^{a_j}(r) Y_{\ell', M'-\frac{1}{2}}^*(\theta, \phi) \left\{ \frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right\} \sqrt{\frac{J-M+1}{2(J+1)}} \\ & \times F_{n\ell J}^{a_i}(r_{ijn}) Y_{\ell, M-\frac{1}{2}}(\theta_{ijn}, \phi_{ijn}) d^3 r \\ & + \int \sqrt{\frac{J'+M'}{2J'}} \frac{1}{rr_{ijn}} \left\{ iG_{n'\ell'J'}^{a_j}(r) \right\}^* Y_{\ell'-1, M'-\frac{1}{2}}^*(\theta, \phi) \left\{ \frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right\} \left\{ \sqrt{\frac{J+M}{2J}} iG_{n\ell J}^{a_i}(r_{ijn}) \right\} \\ & \times Y_{\ell-1, M-\frac{1}{2}}(\theta_{ijn}, \phi_{ijn}) d^3 r \\ & + \int \sqrt{\frac{J'+M'+1}{2(J'+1)}} \frac{1}{rr_{ijn}} F_{n'\ell'J'}^{a_j}(r) Y_{\ell', M'+\frac{1}{2}}^*(\theta, \phi) \left\{ \frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right\} \sqrt{\frac{J+M+1}{2(J+1)}} \\ & \times F_{n\ell J}^{a_i}(r_{ijn}) Y_{\ell, M+\frac{1}{2}}(\theta_{ijn}, \phi_{ijn}) d^3 r \\ & + \int \sqrt{\frac{J'-M'}{2J'}} \frac{1}{rr_{ijn}} \left\{ iG_{n'\ell'J'}^{a_j}(r) \right\}^* Y_{\ell'-1, M'+\frac{1}{2}}^*(\theta, \phi) \left\{ \frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right\} \left\{ \sqrt{\frac{J-M}{2J}} iG_{n\ell J}^{a_i}(r_{ijn}) \right\} \\ & \times Y_{\ell-1, M+\frac{1}{2}}(\theta_{ijn}, \phi_{ijn}) d^3 r \end{aligned} \quad (2.34)$$

where the arguments $(r_{ijn}, \theta_{ijn}, \phi_{ijn})$ stand for the polar coordinates $(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)$. By using Eqs. (2.31), (2.32), (2.33) and (2.34), we should show that $t_{n'\ell'JM', n\ell JM}^{a_j a_i}(\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j)$ can be expressed in terms of $K_d^{a_j a_i}(n'\ell'J', n\ell J)_{|M|}$. Let us derive some relativistic TB parameters:

- (1) Relativistic hopping integral for the combination of $\left(n'0 \frac{1}{2} \frac{1}{2}\right)$ and $\left(n0 \frac{1}{2} \frac{1}{2}\right)$ atomic orbitals:**

Using Eq. (2.31), we have

$$\begin{aligned}
& t_{n'0\frac{11}{22},n0\frac{11}{22}}^{a_j a_i}(\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j) \\
&= \int \frac{1}{rr_{ijn}} F_{n'0\frac{1}{2}}^{a_j}(\mathbf{r})^* Y_{0,0}^*(\theta, \phi) \left\{ \frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right\} F_{n0\frac{1}{2}}^{a_i}(r_{ijn}) Y_{0,0}(\theta_{ijn}, \phi_{ijn}) d^3 r \\
&+ \frac{1}{3} \int \frac{1}{rr_{ijn}} G_{n'0\frac{1}{2}}^{a_j}(\mathbf{r})^* Y_{1,0}^*(\theta, \phi) \left\{ \frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right\} G_{n0\frac{1}{2}}^{a_i}(r_{ijn}) Y_{1,0}(\theta_{ijn}, \phi_{ijn}) d^3 r \\
&+ \frac{2}{3} \int \frac{1}{rr_{ijn}} G_{n'0\frac{1}{2}}^{a_j}(\mathbf{r})^* Y_{1,1}^*(\theta, \phi) \left\{ \frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right\} G_{n0\frac{1}{2}}^{a_i}(r_{ijn}) Y_{1,1}(\theta_{ijn}, \phi_{ijn}) d^3 r. \quad (2.35)
\end{aligned}$$

Let us consider the case in which the atoms are placed along z-axis. In this case, the relativistic hopping integral $t_{n'0\frac{11}{22},n0\frac{11}{22}}^{a_j a_i}(|\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j| \mathbf{e}_z)$ is just equal to $K_d^{a_j a_i} \left(n'0\frac{1}{2}, n0\frac{1}{2} \right)_{1/2}$ from the definition [Eq. (2.27)]. Then we have

$$\begin{aligned}
& K_d^{a_j a_i} \left(n'0\frac{1}{2}, n0\frac{1}{2} \right)_{1/2} \\
&= \int \frac{1}{rr_{ijn}} F_{n'0\frac{1}{2}}^{a_j}(\mathbf{r})^* Y_{0,0}^*(\theta, \phi) \left\{ \frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - |\mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j| \mathbf{e}_z)}{2} \right\} F_{n0\frac{1}{2}}^{a_i}(r_{ijn}^z) Y_{0,0}(\theta_{ijn}^z, \phi) d^3 r \\
&+ \frac{1}{3} \int \frac{1}{rr_{ijn}} G_{n'0\frac{1}{2}}^{a_j}(\mathbf{r})^* Y_{1,0}^*(\theta, \phi) \left\{ \frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - |\mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j| \mathbf{e}_z)}{2} \right\} G_{n0\frac{1}{2}}^{a_i}(r_{ijn}^z) Y_{1,0}(\theta_{ijn}^z, \phi) d^3 r \\
&+ \frac{2}{3} \int \frac{1}{rr_{ijn}} G_{n'0\frac{1}{2}}^{a_j}(\mathbf{r})^* Y_{1,1}^*(\theta, \phi) \left\{ \frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - |\mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j| \mathbf{e}_z)}{2} \right\} G_{n0\frac{1}{2}}^{a_i}(r_{ijn}^z) Y_{1,1}(\theta_{ijn}^z, \phi) d^3 r, \\
&= (ss\sigma)_{(n'0\frac{1}{2}, n0\frac{1}{2})}^{L,d,a_j,a_i} + \frac{1}{3} (pp\sigma)_{(n'0\frac{1}{2}, n0\frac{1}{2})}^{S,d,a_j,a_i} + \frac{2}{3} (pp\pi)_{(n'0\frac{1}{2}, n0\frac{1}{2})}^{S,d,a_j,a_i}, \quad (2.36)
\end{aligned}$$

with

$$(ss\sigma)_{(n'0\frac{1}{2}, n0\frac{1}{2})}^{L,d,a_j,a_i} = \int \frac{1}{rr_{ijn}} F_{n'0\frac{1}{2}}^{a_j}(\mathbf{r})^* Y_{0,0}^*(\theta, \phi) \left\{ \frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - |\mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j| \mathbf{e}_z)}{2} \right\} F_{n0\frac{1}{2}}^{a_i}(r_{ijn}^z) Y_{0,0}(\theta_{ijn}^z, \phi) d^3 r, \quad (2.37)$$

$$\begin{aligned}
(pp\sigma)_{(n'0\frac{1}{2},n0\frac{1}{2})}^{S,d,a_j,a_i} &= \int \frac{1}{rr_{ijn}} G_{n'0\frac{1}{2}}^{a_j}(r) Y_{1,0}^*(\theta, \phi) \left\{ \frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - |\mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j| \mathbf{e}_z)}{2} \right\} G_{n0\frac{1}{2}}^{a_i}(r_{ijn}^z) Y_{1,0}(\theta_{ijn}^z, \phi) d^3r, \\
\end{aligned} \tag{2.38}$$

$$\begin{aligned}
(pp\pi)_{(n'0\frac{1}{2},n0\frac{1}{2})}^{S,d,a_j,a_i} &= \int \frac{1}{rr_{ijn}} G_{n'0\frac{1}{2}}^{a_j}(r) Y_{1,1}^*(\theta, \phi) \left\{ \frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - |\mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j| \mathbf{e}_z)}{2} \right\} G_{n0\frac{1}{2}}^{a_i}(r_{ijn}^z) Y_{1,1}(\theta_{ijn}^z, \phi) d^3r. \\
\end{aligned} \tag{2.39}$$

The subscript L and S in $(ss\sigma)_{(n'0\frac{1}{2},n0\frac{1}{2})}^{L,d,a_j,a_i}$, $(pp\sigma)_{(n'0\frac{1}{2},n0\frac{1}{2})}^{S,d,a_j,a_i}$ and $(pp\pi)_{(n'0\frac{1}{2},n0\frac{1}{2})}^{S,d,a_j,a_i}$ indicate that the integral comes from the large (or small) component of the relativistic atomic orbital. The superscript d has the same meaning as that mentioned above. By convention, the label ℓ' (or ℓ) is denoted by s, p, d, \dots for ℓ' (or ℓ) = 0, 1, 2, \dots respectively, and the label M is denoted by $\sigma, \pi, \delta, \dots$ for $M = 0, \pm 1, \pm 2, \dots$ respectively. It is clear from Eq. (2.36) that $K_d^{a_j a_i} \left(n'0\frac{1}{2}, n0\frac{1}{2} \right)_{1/2}$ contains the contributions that comes from the large and small components of the relativistic atomic orbitals. By using the cubic harmonics (real harmonics) [41] instead of spherical harmonics, Eq. (2.35) can be written as

$$\begin{aligned}
& t_{n'0\frac{1}{2},n0\frac{1}{2}}^{a_j a_i}(\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j) \\
&= \int \frac{1}{rr_{ijn}} F_{n'0\frac{1}{2}}^{a_j}(r) C_s^*(\theta, \phi) \left\{ \frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right\} F_{n0\frac{1}{2}}^{a_i}(r_{ijn}) C_s(\theta_{ijn}, \phi_{ijn}) d^3r \\
&+ \frac{1}{3} \int \frac{1}{rr_{ijn}} G_{n'0\frac{1}{2}}^{a_j}(r) C_z^*(\theta, \phi) \left\{ \frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right\} G_{n0\frac{1}{2}}^{a_i}(r_{ijn}) C_z(\theta_{ijn}, \phi_{ijn}) d^3r \\
&+ \frac{2}{3} \int \frac{1}{rr_{ijn}} G_{n'0\frac{1}{2}}^{a_j}(r) \left\{ -\frac{1}{\sqrt{2}} [C_x(\theta, \phi) + iC_y(\theta, \phi)]^* \right\} \left\{ \frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right\} \\
&\quad \times G_{n0\frac{1}{2}}^{a_i}(r_{ijn}) \left\{ -\frac{1}{\sqrt{2}} [C_x(\theta_{ijn}, \phi_{ijn}) + iC_y(\theta_{ijn}, \phi_{ijn})] \right\} d^3r, \tag{2.40}
\end{aligned}$$

where $C_s(\theta, \phi)$, $C_x(\theta, \phi)$, $C_y(\theta, \phi)$ and $C_z(\theta, \phi)$ denote the cubic harmonics. The definition of which are given by Appendix B. Rearranging the above equations, we get

$$t_{n'0\frac{1}{2},n0\frac{1}{2}}^{a_j a_i}(\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j)$$

$$\begin{aligned}
&= \int \frac{1}{rr_{ijn}} F_{n'0\frac{1}{2}}^{a_j}(r) C_s^*(\theta, \phi) \left\{ \frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right\} F_{n0\frac{1}{2}}^{a_i}(r_{ijn}) C_s(\theta_{ijn}, \phi_{ijn}) d^3r \\
&+ \frac{1}{3} \int \frac{1}{rr_{ijn}} G_{n'0\frac{1}{2}}^{a_j}(r) C_z^*(\theta, \phi) \left\{ \frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right\} G_{n0\frac{1}{2}}^{a_i}(r_{ijn}) C_z(\theta_{ijn}, \phi_{ijn}) d^3r \\
&+ \frac{1}{3} \int \frac{1}{rr_{ijn}} G_{n'0\frac{1}{2}}^{a_j}(r) C_x^*(\theta, \phi) \left\{ \frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right\} G_{n0\frac{1}{2}}^{a_i}(r_{ijn}) C_x(\theta_{ijn}, \phi_{ijn}) d^3r \\
&+ \frac{i}{3} \int \frac{1}{rr_{ijn}} G_{n'0\frac{1}{2}}^{a_j}(r) C_x(\theta, \phi) \left\{ \frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right\} G_{n0\frac{1}{2}}^{a_i}(r_{ijn}) C_y(\theta_{ijn}, \phi_{ijn}) d^3r \\
&- \frac{i}{3} \int \frac{1}{rr_{ijn}} G_{n'0\frac{1}{2}}^{a_j}(r) C_y(\theta, \phi) \left\{ \frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right\} G_{n0\frac{1}{2}}^{a_i}(r_{ijn}) C_y(\theta_{ijn}, \phi_{ijn}) d^3r \\
&+ \frac{1}{3} \int \frac{1}{rr_{ijn}} G_{n'0\frac{1}{2}}^{a_j}(r) C_y(\theta, \phi) \left\{ \frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right\} G_{n0\frac{1}{2}}^{a_i}(r_{ijn}) C_y(\theta_{ijn}, \phi_{ijn}) d^3r \quad (2.41)
\end{aligned}$$

Now applying the non-relativistic Slater-Koster table [40] to each term of the RHS of Eq. (2.41), we have

$$\begin{aligned}
&t_{n'0\frac{1}{2}, n0\frac{1}{2}}^{a_j a_i}(\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j) \\
&= (ss\sigma)_{(n'0\frac{1}{2}, n0\frac{1}{2})}^{L, d, a_j, a_i} + \frac{1}{3} z^2 (pp\sigma)_{(n'0\frac{1}{2}, n0\frac{1}{2})}^{S, d, a_j, a_i} + \frac{1}{3} (1 - z^2) (pp\sigma)_{(n'0\frac{1}{2}, n0\frac{1}{2})}^{S, d, a_j, a_i} + \frac{1}{3} x^2 (pp\pi)_{(n'0\frac{1}{2}, n0\frac{1}{2})}^{S, d, a_j, a_i} \\
&+ \frac{1}{3} (1 - x^2) (pp\pi)_{(n'0\frac{1}{2}, n0\frac{1}{2})}^{S, d, a_j, a_i} + \frac{i}{3} xy \left[(pp\sigma)_{(n'0\frac{1}{2}, n0\frac{1}{2})}^{S, d, a_j, a_i} - (pp\pi)_{(n'0\frac{1}{2}, n0\frac{1}{2})}^{S, d, a_j, a_i} \right] - \frac{i}{3} xy \\
&\times \left[(pp\sigma)_{(n'0\frac{1}{2}, n0\frac{1}{2})}^{S, d, a_j, a_i} - (pp\pi)_{(n'0\frac{1}{2}, n0\frac{1}{2})}^{S, d, a_j, a_i} \right] + \frac{1}{3} y^2 (pp\pi)_{(n'0\frac{1}{2}, n0\frac{1}{2})}^{S, d, a_j, a_i} + \frac{1}{3} (1 - y^2) (pp\pi)_{(n'0\frac{1}{2}, n0\frac{1}{2})}^{S, d, a_j, a_i} \\
&= (ss\sigma)_{(n'0\frac{1}{2}, n0\frac{1}{2})}^{L, d, a_j, a_i} + \frac{1}{3} (pp\sigma)_{(n'0\frac{1}{2}, n0\frac{1}{2})}^{S, d, a_j, a_i} + \frac{2}{3} (pp\pi)_{(n'0\frac{1}{2}, n0\frac{1}{2})}^{S, d, a_j, a_i}. \quad (2.42)
\end{aligned}$$

Comparing Eqs. (2.36) and (2.42), we get

$$t_{n'0\frac{11}{22},n0\frac{11}{22}}^{a_j a_i}(\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j) = K_d^{a_j a_i} \left(n'0\frac{1}{2}, n0\frac{1}{2} \right)_{1/2}. \quad (2.43)$$

(2) Relativistic hopping integral for the combination of $\left(n'0\frac{1}{2} \right)$ and $\left(n1\frac{1}{2} \right)$ atomic orbitals:

From Eq. (2.32), we have

$$\begin{aligned} t_{n'0\frac{11}{22},n1\frac{11}{22}}^{a_j a_i}(\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j) = & \\ & -\frac{1}{\sqrt{3}} \int \frac{1}{r r_{ijn}} F_{n'0\frac{1}{2}}^{a_j}(r) Y_{0,0}^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] F_{n1\frac{1}{2}}^{a_i}(r_{ijn}) Y_{1,0}(\theta_{ijn}, \phi_{ijn}) d^3 r \\ & -\frac{1}{\sqrt{3}} \int \frac{1}{r r_{ijn}} G_{n'0\frac{1}{2}}^{a_j}(r) Y_{1,0}^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] G_{n1\frac{1}{2}}^{a_i}(r_{ijn}) Y_{0,0}(\theta_{ijn}, \phi_{ijn}) d^3 r, \end{aligned} \quad (2.44)$$

According to the definition of relativistic TB parameter [Eq. (2.27)], we have

$$\begin{aligned} K_d^{a_j a_i} \left(n'0\frac{1}{2}, n1\frac{1}{2} \right)_{1/2} & \\ = -\frac{1}{\sqrt{3}} \int \frac{1}{r r_{ijn}} F_{n'0\frac{1}{2}}^{a_j}(r) Y_{0,0}^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - |\mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j| \mathbf{e}_z)}{2} \right] F_{n1\frac{1}{2}}^{a_i}(r_{ijn}^z) Y_{1,0}(\theta_{ijn}^z, \phi) d^3 r & \\ -\frac{1}{\sqrt{3}} \int \frac{1}{r r_{ijn}} G_{n'0\frac{1}{2}}^{a_j}(r) Y_{1,0}^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - |\mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j| \mathbf{e}_z)}{2} \right] G_{n1\frac{1}{2}}^{a_i}(r_{ijn}^z) Y_{0,0}(\theta_{ijn}^z, \phi) d^3 r & \\ = -\frac{1}{\sqrt{3}} (sp\sigma)_{(n'0\frac{1}{2}, n1\frac{1}{2})}^{L,d,a_j,a_i} - \frac{1}{\sqrt{3}} (ps\sigma)_{(n'0\frac{1}{2}, n1\frac{1}{2})}^{S,d,a_j,a_i}. & \end{aligned} \quad (2.45)$$

By using the cubic harmonics, Eq. (2.44) can be written as

$$t_{n'0\frac{11}{22},n1\frac{11}{22}}^{a_j a_i}(\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j) =$$

$$\begin{aligned}
& -\frac{1}{\sqrt{3}} \int \frac{1}{r r_{ijn}} F_{n'0\frac{1}{2}}^{a_j}(r) C_s^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] F_{n1\frac{1}{2}}^{a_i}(r_{ijn}) C_z(\theta_{ijn}, \phi_{ijn}) d^3 r \\
& -\frac{1}{\sqrt{3}} \int \frac{1}{r r_{ijn}} G_{n'0\frac{1}{2}}^{a_j}(r) C_z^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] G_{n1\frac{1}{2}}^{a_i}(r_{ijn}) C_s(\theta_{ijn}, \phi_{ijn}) d^3 r \quad (2.46)
\end{aligned}$$

Now applying the result of Slater-Koster table [40] to each term of the RHS of Eq. (2.46), we have

$$\begin{aligned}
& = -\frac{1}{\sqrt{3}} z (sp\sigma)_{(n'0\frac{1}{2}, n1\frac{1}{2})}^{L,d,a_j,a_i} - \frac{1}{\sqrt{3}} z (ps\sigma)_{(n'0\frac{1}{2}, n1\frac{1}{2})}^{S,d,a_j,a_i} \\
& = z \left\{ -\frac{1}{\sqrt{3}} (sp\sigma)_{(n'0\frac{1}{2}, n1\frac{1}{2})}^{L,d,a_j,a_i} - \frac{1}{\sqrt{3}} (ps\sigma)_{(n'0\frac{1}{2}, n1\frac{1}{2})}^{S,d,a_j,a_i} \right\}. \quad (2.47)
\end{aligned}$$

Comparing Eqs. (2.45) and (2.47), we get

$$t_{n'0\frac{11}{22}, n1\frac{11}{22}}^{a_j a_i}(\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j) = z K_d^{a_j a_i} \left(n'0\frac{1}{2}, n1\frac{1}{2} \right)_{1/2} \quad (2.48)$$

(3) Relativistic hopping integral for the combination of $\left(n'0\frac{1}{2} \frac{1}{2} \right)$ and $\left(n1\frac{3}{2} \frac{1}{2} \right)$ atomic orbitals:

From Eq. (2.31), we have

$$\begin{aligned}
& t_{n'0\frac{11}{22}, n1\frac{31}{22}}^{a_j a_i}(\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j) \\
& = \sqrt{\frac{2}{3}} \int \frac{1}{r r_{ijn}} F_{n'0\frac{1}{2}}^{a_j}(r) Y_{0,0}^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] F_{n1\frac{3}{2}}^{a_i}(r_{ijn}) Y_{1,0}(\theta_{ijn}, \phi_{ijn}) d^3 r \\
& + \sqrt{\frac{2}{15}} \int \frac{1}{r r_{ijn}} G_{n'0\frac{1}{2}}^{a_j}(r) Y_{1,0}^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] G_{n1\frac{3}{2}}^{a_i}(r_{ijn}) Y_{2,0}(\theta_{ijn}, \phi_{ijn}) d^3 r \\
& + \sqrt{\frac{2}{5}} \int \frac{1}{r r_{ijn}} G_{n'0\frac{1}{2}}^{a_j}(r) Y_{1,1}^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] G_{n1\frac{3}{2}}^{a_i}(r_{ijn}) Y_{2,1}(\theta_{ijn}, \phi_{ijn}) d^3 r \quad (2.49)
\end{aligned}$$

According to the definition of relativistic TB parameter [Eq. (2.27)], we have

$$\begin{aligned}
& K_d^{a_j a_i} \left(n'0 \frac{1}{2}, n1 \frac{3}{2} \right)_{1/2} \\
&= \sqrt{\frac{2}{3}} \int \frac{1}{r r_{ijn}} F_{n'0 \frac{1}{2}}^{a_j}(r) Y_{0,0}^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - |\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j| \mathbf{e}_z)}{2} \right] F_{n1 \frac{3}{2}}^{a_i}(r_{ijn}^z) Y_{1,0}(\theta_{ijn}^z, \phi) d^3 r \\
&+ \sqrt{\frac{2}{15}} \int \frac{1}{r r_{ijn}} G_{n'0 \frac{1}{2}}^{a_j}(r) Y_{1,0}^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - |\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j| \mathbf{e}_z)}{2} \right] G_{n1 \frac{3}{2}}^{a_i}(r_{ijn}^z) Y_{2,0}(\theta_{ijn}^z, \phi) d^3 r \\
&+ \sqrt{\frac{2}{5}} \int \frac{1}{r r_{ijn}} G_{n'0 \frac{1}{2}}^{a_j}(r) Y_{1,1}^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - |\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j| \mathbf{e}_z)}{2} \right] G_{n1 \frac{3}{2}}^{a_i}(r_{ijn}^z) Y_{2,1}(\theta_{ijn}^z, \phi) d^3 r \\
&= \sqrt{\frac{2}{3}} (sp\sigma)_{(n'0 \frac{1}{2}, n1 \frac{3}{2})}^{L,d,a_j,a_i} + \sqrt{\frac{2}{15}} (pd\sigma)_{(n'0 \frac{1}{2}, n1 \frac{3}{2})}^{S,d,a_j,a_i} + \sqrt{\frac{2}{5}} (pd\pi)_{(n'0 \frac{1}{2}, n1 \frac{3}{2})}^{S,d,a_j,a_i}. \tag{2.50}
\end{aligned}$$

By using cubic harmonics, Eq. (2.49) can be written as

$$\begin{aligned}
& t_{n'0 \frac{11}{22}, n1 \frac{31}{22}}^{a_j a_i}(\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j) \\
&= \sqrt{\frac{2}{3}} \int \frac{1}{r r_{ijn}} F_{n'0 \frac{1}{2}}^{a_j}(r) C_s^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] F_{n1 \frac{3}{2}}^{a_i}(r_{ijn}) C_z(\theta_{ijn}, \phi_{ijn}) d^3 r \\
&+ \sqrt{\frac{2}{15}} \int \frac{1}{r r_{ijn}} G_{n'0 \frac{1}{2}}^{a_j}(r) C_z^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] G_{n1 \frac{3}{2}}^{a_i}(r_{ijn}) C_{3z^2-r^2}(\theta_{ijn}, \phi_{ijn}) d^3 r \\
&+ \sqrt{\frac{2}{5}} \int \frac{1}{r r_{ijn}} G_{n'0 \frac{1}{2}}^{a_j}(r) \left\{ -\frac{1}{\sqrt{2}} [C_x(\theta, \phi) + iC_y(\theta, \phi)] \right\}^* \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] \\
&\quad \times G_{n1 \frac{3}{2}}^{a_i}(r_{ijn}) \left\{ -\frac{1}{\sqrt{2}} [C_{xz}(\theta_{ijn}, \phi_{ijn}) + iC_{yz}(\theta_{ijn}, \phi_{ijn})] \right\} d^3 r \tag{2.51}
\end{aligned}$$

Rearranging Eq. (2.51), we have

$$t_{n'0 \frac{11}{22}, n1 \frac{31}{22}}^{a_j a_i}(\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j)$$

$$\begin{aligned}
&= \sqrt{\frac{2}{3}} \int \frac{1}{r r_{ijn}} F_{n'0\frac{1}{2}}^{a_j}(\mathbf{r})^* C_s^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] F_{n\frac{1}{2}}^{a_i}(r_{ijn}) C_z(\theta_{ijn}, \phi_{ijn}) d^3 r \\
&+ \sqrt{\frac{2}{15}} \int \frac{1}{r r_{ijn}} G_{n'0\frac{1}{2}}^{a_j}(\mathbf{r})^* C_z^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] G_{n\frac{1}{2}}^{a_i}(r_{ijn}) C_{3z^2-r^2}(\theta_{ijn}, \phi_{ijn}) d^3 r \\
&+ \frac{1}{10} \int \frac{1}{r r_{ijn}} G_{n'0\frac{1}{2}}^{a_j}(\mathbf{r})^* C_z^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] G_{n\frac{1}{2}}^{a_i}(r_{ijn}) C_{3z^2-r^2}(\theta_{ijn}, \phi_{ijn}) d^3 r \\
&+ i \sqrt{\frac{1}{10}} \int \frac{1}{r r_{ijn}} G_{n'0\frac{1}{2}}^{a_j}(\mathbf{r})^* C_x^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] G_{n\frac{1}{2}}^{a_i}(r_{ijn}) C_{yz}(\theta_{ijn}, \phi_{ijn}) d^3 r \\
&- i \sqrt{\frac{1}{10}} \int \frac{1}{r r_{ijn}} G_{n'0\frac{1}{2}}^{a_j}(\mathbf{r})^* C_y^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] G_{n\frac{1}{2}}^{a_i}(r_{ijn}) C_{xz}(\theta_{ijn}, \phi_{ijn}) d^3 r \\
&+ \sqrt{\frac{1}{10}} \int \frac{1}{r r_{ijn}} G_{n'0\frac{1}{2}}^{a_j}(\mathbf{r})^* C_y^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] G_{n\frac{1}{2}}^{a_i}(r_{ijn}) C_{yz}(\theta_{ijn}, \phi_{ijn}) d^3 r
\end{aligned} \tag{2.52}$$

Now applying the result of Slater-Koster table [40] to each term of the RHS of Eq. (2.52), we have

$$\begin{aligned}
&t_{n'0\frac{1}{2}2, n\frac{1}{2}\frac{3}{2}}^{a_j a_i}(\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j) \\
&= \sqrt{\frac{2}{3}} z (sp\sigma)_{(n'0\frac{1}{2}, n\frac{1}{2}\frac{3}{2})}^{L, d, a_j, a_i} + \sqrt{\frac{2}{15}} \left\{ z \left[z^2 - \frac{1}{2}(x^2 + y^2) \right] (pd\sigma)_{(n'0\frac{1}{2}, n\frac{1}{2}\frac{3}{2})}^{S, d, a_j, a_i} + \sqrt{3} z(x^2 + y^2) (pd\pi)_{(n'0\frac{1}{2}, n\frac{1}{2}\frac{3}{2})}^{S, d, a_j, a_i} \right\} \\
&+ \sqrt{\frac{1}{10}} \left\{ \sqrt{3} x^2 z (pd\sigma)_{(n'0\frac{1}{2}, n\frac{1}{2}\frac{3}{2})}^{S, d, a_j, a_i} + z(1 - 2x^2) (pd\pi)_{(n'0\frac{1}{2}, n\frac{1}{2}\frac{3}{2})}^{S, d, a_j, a_i} \right\} + i \sqrt{\frac{1}{10}} \left\{ \sqrt{3} xyz (pd\sigma)_{(n'0\frac{1}{2}, n\frac{1}{2}\frac{3}{2})}^{S, d, a_j, a_i} - 2xy \right. \\
&\times (pd\pi)_{(n'0\frac{1}{2}, n\frac{1}{2}\frac{3}{2})}^{S, d, a_j, a_i} \left. \right\} - i \sqrt{\frac{1}{10}} \left\{ \sqrt{3} xyz (pd\sigma)_{(n'0\frac{1}{2}, n\frac{1}{2}\frac{3}{2})}^{S, d, a_j, a_i} - 2xyz (pd\pi)_{(n'0\frac{1}{2}, n\frac{1}{2}\frac{3}{2})}^{S, d, a_j, a_i} \right\} + \sqrt{\frac{1}{10}} \left\{ \sqrt{3} y^2 z (pd\sigma)_{(n'0\frac{1}{2}, n\frac{1}{2}\frac{3}{2})}^{S, d, a_j, a_i} \right. \\
&+ z(1 - 2y^2) (pd\pi)_{(n'0\frac{1}{2}, n\frac{1}{2}\frac{3}{2})}^{S, d, a_j, a_i} \left. \right\} \\
&= z \left\{ \sqrt{\frac{2}{3}} (sp\sigma)_{(n'0\frac{1}{2}, n\frac{1}{2}\frac{3}{2})}^{L, d, a_j, a_i} + \sqrt{\frac{2}{15}} (pd\sigma)_{(n'0\frac{1}{2}, n\frac{1}{2}\frac{3}{2})}^{S, d, a_j, a_i} + \sqrt{\frac{2}{5}} (pd\pi)_{(n'0\frac{1}{2}, n\frac{1}{2}\frac{3}{2})}^{S, d, a_j, a_i} \right\}. \tag{2.53}
\end{aligned}$$

Comparing Eqs. (2.50) and (2.53), we get

$$t_{n'0\frac{1}{2},n1\frac{3}{2}}^{a_j a_i}(\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j) = z K_d^{a_j a_i} \left(n'0\frac{1}{2}, n1\frac{3}{2} \right)_{1/2}. \quad (2.54)$$

(4) Relativistic TB parameter for the combination of $\left(n'1\frac{1}{2} \frac{1}{2} \right)$ and $\left(n0\frac{1}{2} \frac{1}{2} \right)$ atomic orbitals:

From Eq. (2.33), we have

$$\begin{aligned} & t_{n'1\frac{1}{2},n0\frac{1}{2}}^{a_j a_i}(\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j) \\ &= -\frac{1}{\sqrt{3}} \int \frac{1}{r r_{ijn}} F_{n'1\frac{1}{2}}^{a_j}(r) Y_{1,0}^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] F_{n0\frac{1}{2}}^{a_i}(r_{ijn}) Y_{0,0}(\theta_{ijn}, \phi_{ijn}) d^3 r \\ & - \frac{1}{\sqrt{3}} \int \frac{1}{r r_{ijn}} G_{n'1\frac{1}{2}}^{a_j}(r) Y_{0,0}^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] G_{n0\frac{1}{2}}^{a_i}(r_{ijn}) Y_{1,0}(\theta_{ijn}, \phi_{ijn}) d^3 r \end{aligned} \quad (2.55)$$

According to the definition of relativistic TB parameter [Eq. (2.27)], we have

$$\begin{aligned} & K_d^{a_j a_i} \left(n'1\frac{1}{2}, n0\frac{1}{2} \right)_{1/2} \\ &= -\frac{1}{\sqrt{3}} \int \frac{1}{r r_{ijn}} F_{n'1\frac{1}{2}}^{a_j}(r) Y_{1,0}^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - |\mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j| \mathbf{e}_z)}{2} \right] F_{n0\frac{1}{2}}^{a_i}(r_{ijn}^z) Y_{0,0}(\theta_{ijn}^z, \phi) d^3 r \\ & - \frac{1}{\sqrt{3}} \int \frac{1}{r r_{ijn}} G_{n'1\frac{1}{2}}^{a_j}(r) Y_{0,0}^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - |\mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j| \mathbf{e}_z)}{2} \right] G_{n0\frac{1}{2}}^{a_i}(r_{ijn}^z) Y_{1,0}(\theta_{ijn}^z, \phi) d^3 r \\ &= -\frac{1}{\sqrt{3}} (ps\sigma)_{(n'1\frac{1}{2}, n0\frac{1}{2})}^{L,d,a_j,a_i} - \frac{1}{\sqrt{3}} (sp\sigma)_{(n'1\frac{1}{2}, n0\frac{1}{2})}^{S,d,a_j,a_i}, \end{aligned} \quad (2.56)$$

with

$$(ps\sigma)_{(n'1\frac{1}{2}, n0\frac{1}{2})}^{L,d,a_j,a_i} = \int \frac{1}{r r_{ijn}} F_{n'1\frac{1}{2}}^{a_j}(r) Y_{1,0}^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - |\mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j| \mathbf{e}_z)}{2} \right] F_{n0\frac{1}{2}}^{a_i}(r_{ijn}) Y_{0,0}(\theta_{ijn}, \phi_{ijn}) d^3 r.$$

By using cubic harmonics, Eq. (2.55) can be written as

$$\begin{aligned}
& t_{n'1\frac{11}{22},n0\frac{11}{22}}^{a_j a_i}(\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j) \\
&= -\frac{1}{\sqrt{3}} \int \frac{1}{r r_{ijn}} F_{n'1\frac{1}{2}}^{a_j}(r) C_z^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] F_{n0\frac{1}{2}}^{a_i}(r_{ijn}) C_s(\theta_{ijn}, \phi_{ijn}) d^3 r \\
& -\frac{1}{\sqrt{3}} \int \frac{1}{r r_{ijn}} G_{n'1\frac{1}{2}}^{a_j}(r) C_s^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] G_{n0\frac{1}{2}}^{a_i}(r_{ijn}) C_z(\theta_{ijn}, \phi_{ijn}) d^3 r \quad (2.57)
\end{aligned}$$

Now applying the result of Slater-Koster table [40] to each term of the RHS of Eq. (2.57), we have

$$\begin{aligned}
&= -\frac{1}{\sqrt{3}} z (ps\sigma)_{(n'1\frac{1}{2}, n0\frac{1}{2})}^{L,d,a_j,a_i} - \frac{1}{\sqrt{3}} z (sp\sigma)_{(n'1\frac{1}{2}, n0\frac{1}{2})}^{S,d,a_j,a_i} \\
&= z \left\{ -\frac{1}{\sqrt{3}} (ps\sigma)_{(n'1\frac{1}{2}, n0\frac{1}{2})}^{L,d,a_j,a_i} - \frac{1}{\sqrt{3}} (sp\sigma)_{(n'1\frac{1}{2}, n0\frac{1}{2})}^{S,d,a_j,a_i} \right\}. \quad (2.58)
\end{aligned}$$

Comparing Eqs. (2.56) and (2.58), we get

$$t_{n'1\frac{11}{22},n0\frac{11}{22}}^{a_j a_i}(\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j) = z K_d^{a_j a_i} \left(n'1\frac{1}{2}, n0\frac{1}{2} \right)_{1/2}. \quad (2.59)$$

(5) Relativistic hopping integral for the combination of $\left(n'1\frac{1}{2} \frac{1}{2} \right)$ and $\left(n1\frac{1}{2} \frac{1}{2} \right)$ atomic orbitals:

From Eq. (2.34), we have

$$\begin{aligned}
& t_{n'1\frac{11}{22},n1\frac{11}{22}}^{a_j a_i}(\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j) \\
&= \frac{1}{3} \int \frac{1}{r r_{ijn}} F_{n'1\frac{1}{2}}^{a_j}(r) Y_{1,0}^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] F_{n1\frac{1}{2}}^{a_i}(r_{ijn}) Y_{1,0}(\theta_{ijn}, \phi_{ijn}) d^3 r \\
& + \frac{2}{3} \int \frac{1}{r r_{ijn}} F_{n'1\frac{1}{2}}^{a_j}(r) Y_{1,1}^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] F_{n1\frac{1}{2}}^{a_i}(r_{ijn}) Y_{1,1}(\theta_{ijn}, \phi_{ijn}) d^3 r
\end{aligned}$$

$$+\int \frac{1}{r r_{ijn}} G_{n'1\frac{1}{2}}^{a_j}(r) Y_{0,0}^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] G_{n1\frac{1}{2}}^{a_i}(r_{ijn}) Y_{0,0}(\theta_{ijn}, \phi_{ijn}) d^3 r \quad (2.60)$$

According to the definition of relativistic TB parameter [Eq. (2.27)], we have

$$\begin{aligned} & K_d^{a_j a_i} \left(n'1\frac{1}{2}, n1\frac{1}{2} \right)_{1/2} \\ &= \frac{1}{3} \int \frac{1}{r r_{ijn}} F_{n'1\frac{1}{2}}^{a_j}(r) Y_{1,0}^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(|\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j| \mathbf{e}_z)}{2} \right] F_{n1\frac{1}{2}}^{a_i}(r_{ijn}^z) Y_{1,0}(\theta_{ijn}^z, \phi) d^3 r \\ &+ \frac{2}{3} \int \frac{1}{r r_{ijn}} F_{n'1\frac{1}{2}}^{a_j}(r) Y_{1,1}^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(|\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j| \mathbf{e}_z)}{2} \right] F_{n1\frac{1}{2}}^{a_i}(r_{ijn}^z) Y_{1,1}(\theta_{ijn}^z, \phi) d^3 r \\ &+ \int \frac{1}{r r_{ijn}} G_{n'1\frac{1}{2}}^{a_j}(r) Y_{0,0}^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(|\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j| \mathbf{e}_z)}{2} \right] G_{n1\frac{1}{2}}^{a_i}(r_{ijn}^z) Y_{0,0}(\theta_{ijn}^z, \phi) d^3 r \\ &= \frac{1}{3} (pp\sigma)_{(n'1\frac{1}{2}, n1\frac{1}{2})}^{L,d,a_j,a_i} + \frac{2}{3} (pp\pi)_{(n'1\frac{1}{2}, n1\frac{1}{2})}^{L,d,a_j,a_i} + (ss\sigma)_{(n'1\frac{1}{2}, n1\frac{1}{2})}^{S,d,a_j,a_i}. \end{aligned} \quad (2.61)$$

Using cubic harmonics, Eq. (2.60) can be written as

$$\begin{aligned} & t_{n'1\frac{1}{2}, n1\frac{1}{2}}^{a_j a_i}(\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j) \\ &= \frac{1}{3} \int \frac{1}{r r_{ijn}} F_{n'1\frac{1}{2}}^{a_j}(r) C_z^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] F_{n1\frac{1}{2}}^{a_i}(r_{ijn}) C_z(\theta_{ijn}, \phi_{ijn}) d^3 r \\ &+ \frac{2}{3} \int \frac{1}{r r_{ijn}} F_{n'1\frac{1}{2}}^{a_j}(r) \left\{ -\frac{1}{\sqrt{2}} [C_x(\theta, \phi) + iC_y(\theta, \phi)] \right\}^* \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] \\ &\quad \times F_{n1\frac{1}{2}}^{a_i}(r_{ijn}) \left\{ -\frac{1}{\sqrt{2}} [C_x(\theta_{ijn}, \phi_{ijn}) + iC_y(\theta_{ijn}, \phi_{ijn})] \right\} d^3 r \\ &+ \int \frac{1}{r r_{ijn}} G_{n'1\frac{1}{2}}^{a_j}(r) C_s^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] G_{n1\frac{1}{2}}^{a_i}(r_{ijn}) C_s(\theta_{ijn}, \phi_{ijn}) d^3 r \end{aligned} \quad (2.62)$$

Rearranging Eq. (2.62), we have

$$\begin{aligned}
& t_{n'1\frac{1}{2},n1\frac{1}{2}}^{a_j a_i}(\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j) \\
&= \frac{1}{3} \int \frac{1}{r r_{ijn}} F_{n'1\frac{1}{2}}^{a_j}(\mathbf{r})^* C_z^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] F_{n1\frac{1}{2}}^{a_i}(\mathbf{r}_{ijn}) C_z(\theta_{ijn}, \phi_{ijn}) d^3 r \\
&+ \frac{1}{3} \int \frac{1}{r r_{ijn}} F_{n'1\frac{1}{2}}^{a_j}(\mathbf{r})^* C_x^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] F_{n1\frac{1}{2}}^{a_i}(\mathbf{r}_{ijn}) C_x(\theta_{ijn}, \phi_{ijn}) d^3 r \\
&+ i \frac{1}{3} \int \frac{1}{r r_{ijn}} F_{n'1\frac{1}{2}}^{a_j}(\mathbf{r})^* C_x^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] F_{n1\frac{1}{2}}^{a_i}(\mathbf{r}_{ijn}) C_y(\theta_{ijn}, \phi_{ijn}) d^3 r \\
&- i \frac{1}{3} \int \frac{1}{r r_{ijn}} F_{n'1\frac{1}{2}}^{a_j}(\mathbf{r})^* C_y^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] F_{n1\frac{1}{2}}^{a_i}(\mathbf{r}_{ijn}) C_x(\theta_{ijn}, \phi_{ijn}) d^3 r \\
&+ \frac{1}{3} \int \frac{1}{r r_{ijn}} F_{n'1\frac{1}{2}}^{a_j}(\mathbf{r})^* C_y^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] F_{n1\frac{1}{2}}^{a_i}(\mathbf{r}_{ijn}) C_y(\theta_{ijn}, \phi_{ijn}) d^3 r \\
&+ \int \frac{1}{r r_{ijn}} G_{n'1\frac{1}{2}}^{a_j}(\mathbf{r})^* C_s^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] G_{n1\frac{1}{2}}^{a_i}(\mathbf{r}_{ijn}) C_s(\theta_{ijn}, \phi_{ijn}) d^3 r \quad (2.63)
\end{aligned}$$

Now applying the result of Slater-Koster table [40] to each term of the RHS of Eq. (2.63), we have

$$\begin{aligned}
& t_{n'1\frac{1}{2},n1\frac{1}{2}}^{a_j a_i}(\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j) \\
&= \frac{1}{3} z^2 (pp\sigma)_{(n'1\frac{1}{2},n1\frac{1}{2})}^{L,d,a_j,a_i} + \frac{1}{3} (1-z^2) (pp\pi)_{(n'1\frac{1}{2},n1\frac{1}{2})}^{L,d,a_j,a_i} + \frac{1}{3} x^2 (pp\sigma)_{(n'1\frac{1}{2},n1\frac{1}{2})}^{L,d,a_j,a_i} + \frac{1}{3} (1-x^2) (pp\pi)_{(n'1\frac{1}{2},n1\frac{1}{2})}^{L,d,a_j,a_i} \\
&+ \frac{i}{3} \left\{ xy \left[(pp\sigma)_{(n'1\frac{1}{2},n1\frac{1}{2})}^{L,d,a_j,a_i} - (pp\pi)_{(n'1\frac{1}{2},n1\frac{1}{2})}^{L,d,a_j,a_i} \right] - \frac{i}{3} \left\{ xy \left[(pp\sigma)_{(n'1\frac{1}{2},n1\frac{1}{2})}^{L,d,a_j,a_i} - (pp\pi)_{(n'1\frac{1}{2},n1\frac{1}{2})}^{L,d,a_j,a_i} \right] + \frac{1}{3} y^2 \right. \right. \\
&\times (pp\sigma)_{(n'1\frac{1}{2},n1\frac{1}{2})}^{L,d,a_j,a_i} + \frac{1}{3} (1-y^2) (pp\pi)_{(n'1\frac{1}{2},n1\frac{1}{2})}^{L,d,a_j,a_i} + (ss\sigma)_{(n'1\frac{1}{2},n1\frac{1}{2})}^{S,d,a_j,a_i} \\
&= \frac{1}{3} (pp\sigma)_{(n'1\frac{1}{2},n1\frac{1}{2})}^{L,d,a_j,a_i} + \frac{2}{3} (pp\pi)_{(n'1\frac{1}{2},n1\frac{1}{2})}^{L,d,a_j,a_i} + (ss\sigma)_{(n'1\frac{1}{2},n1\frac{1}{2})}^{S,d,a_j,a_i} \quad (2.64)
\end{aligned}$$

Comparing Eqs. (2.61) and (2.64), we get

$$t_{n'l\frac{1}{2},n'l\frac{1}{2}}^{a_j a_i}(\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j) = K_d^{a_j a_i} \left(n'l\frac{1}{2}, n'l\frac{1}{2} \right)_{1/2}. \quad (2.65)$$

(6) **Relativistic hopping integral for the combination of $\left(n'l\frac{1}{2} \right)$ and $\left(n'l\frac{3}{2} \right)$ atomic orbitals:**

From Eq. (2.33), we have

$$\begin{aligned} & t_{n'l\frac{1}{2},n'l\frac{3}{2}}^{a_j a_i}(\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j) \\ &= -\frac{\sqrt{2}}{3} \int \frac{1}{r r_{ijn}} F_{n'l\frac{1}{2}}^{a_j}(r) Y_{1,0}^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] F_{n'l\frac{3}{2}}^{a_i}(r_{ijn}) Y_{1,0}(\theta_{ijn}, \phi_{ijn}) d^3 r \\ &+ \frac{\sqrt{2}}{3} \int \frac{1}{r r_{ijn}} F_{n'l\frac{1}{2}}^{a_j}(r) Y_{1,1}^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] F_{n'l\frac{3}{2}}^{a_i}(r_{ijn}) Y_{1,1}(\theta_{ijn}, \phi_{ijn}) d^3 r \\ &+ \sqrt{\frac{2}{5}} \int \frac{1}{r r_{ijn}} G_{n'l\frac{1}{2}}^{a_j}(r) Y_{0,0}^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] G_{n'l\frac{3}{2}}^{a_i}(r_{ijn}) Y_{2,0}(\theta_{ijn}, \phi_{ijn}) d^3 r \end{aligned} \quad (2.66)$$

According to the definition of relativistic TB parameter [Eq. (2.27)], we have

$$\begin{aligned} & K_d^{a_j a_i} \left(n'l\frac{1}{2}, n'l\frac{3}{2} \right)_{1/2} \\ &= -\frac{\sqrt{2}}{3} \int \frac{1}{r r_{ijn}} F_{n'l\frac{1}{2}}^{a_j}(r) Y_{1,0}^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(|\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j| \mathbf{e}_z)}{2} \right] F_{n'l\frac{3}{2}}^{a_i}(r_{ijn}^z) Y_{1,0}(\theta_{ijn}^z, \phi) d^3 r \\ &+ \frac{\sqrt{2}}{3} \int \frac{1}{r r_{ijn}} F_{n'l\frac{1}{2}}^{a_j}(r) Y_{1,1}^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(|\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j| \mathbf{e}_z)}{2} \right] F_{n'l\frac{3}{2}}^{a_i}(r_{ijn}^z) Y_{1,1}(\theta_{ijn}^z, \phi) d^3 r \\ &+ \sqrt{\frac{2}{5}} \int \frac{1}{r r_{ijn}} G_{n'l\frac{1}{2}}^{a_j}(r) Y_{0,0}^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(|\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j| \mathbf{e}_z)}{2} \right] G_{n'l\frac{3}{2}}^{a_i}(r_{ijn}^z) Y_{2,0}(\theta_{ijn}^z, \phi) d^3 r \\ &= -\frac{\sqrt{2}}{3} (pp\sigma)_{(n'l\frac{1}{2}, n'l\frac{3}{2})}^{L,d,a_j,a_i} + \frac{\sqrt{2}}{3} (pp\pi)_{(n'l\frac{1}{2}, n'l\frac{3}{2})}^{L,d,a_j,a_i} - \sqrt{\frac{2}{5}} (sd\sigma)_{(n'l\frac{1}{2}, n'l\frac{3}{2})}^{S,d,a_j,a_i} \end{aligned} \quad (2.67)$$

By using cubic harmonics, Eq. (2.66) can be written as

$$\begin{aligned}
& t_{n^1 \frac{11}{22}, n^1 \frac{31}{22}}^{a_j a_i} (\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j) \\
&= -\frac{\sqrt{2}}{3} \int \frac{1}{r r_{ijn}} F_{n^1 \frac{1}{2}}^{a_j}(r) C_z^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] F_{n^1 \frac{3}{2}}^{a_i}(r_{ijn}) C_z(\theta_{ijn}, \phi_{ijn}) d^3 r \\
&+ \frac{\sqrt{2}}{3} \int \frac{1}{r r_{ijn}} F_{n^1 \frac{1}{2}}^{a_j}(r) \left\{ -\frac{1}{\sqrt{2}} [C_x(\theta, \phi) + i C_y(\theta, \phi)] \right\}^* \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] \\
&\quad \times F_{n^1 \frac{3}{2}}^{a_i}(r_{ijn}) \left\{ -\frac{1}{\sqrt{2}} [C_x(\theta_{ijn}, \phi_{ijn}) + i C_y(\theta_{ijn}, \phi_{ijn})] \right\} d^3 r \\
&- \sqrt{\frac{2}{5}} \int \frac{1}{r r_{ijn}} G_{n^1 \frac{1}{2}}^{a_j}(r) C_s^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] G_{n^1 \frac{3}{2}}^{a_i}(r_{ijn}) C_{3z^2-r^2}(\theta_{ijn}, \phi_{ijn}) d^3 r
\end{aligned} \tag{2.68}$$

Rearranging Eq. (2.68), we have

$$\begin{aligned}
& t_{n^1 \frac{11}{22}, n^1 \frac{31}{22}}^{a_j a_i} (\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j) \\
&= -\frac{\sqrt{2}}{3} \int \frac{1}{r r_{ijn}} F_{n^1 \frac{1}{2}}^{a_j}(r) C_z^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] F_{n^1 \frac{3}{2}}^{a_i}(r_{ijn}) C_z(\theta_{ijn}, \phi_{ijn}) d^3 r \\
&+ \frac{1}{3\sqrt{2}} \int \frac{1}{r r_{ijn}} F_{n^1 \frac{1}{2}}^{a_j}(r) C_x^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] F_{n^1 \frac{3}{2}}^{a_i}(r_{ijn}) C_x(\theta_{ijn}, \phi_{ijn}) d^3 r \\
&+ i \frac{1}{3\sqrt{2}} \int \frac{1}{r r_{ijn}} F_{n^1 \frac{1}{2}}^{a_j}(r) C_x^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] F_{n^1 \frac{3}{2}}^{a_i}(r_{ijn}) C_y(\theta_{ijn}, \phi_{ijn}) d^3 r \\
&- i \frac{1}{3\sqrt{2}} \int \frac{1}{r r_{ijn}} F_{n^1 \frac{1}{2}}^{a_j}(r) C_y^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] F_{n^1 \frac{3}{2}}^{a_i}(r_{ijn}) C_x(\theta_{ijn}, \phi_{ijn}) d^3 r \\
&+ \frac{1}{3\sqrt{2}} \int \frac{1}{r r_{ijn}} F_{n^1 \frac{1}{2}}^{a_j}(r) C_y^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] F_{n^1 \frac{3}{2}}^{a_i}(r_{ijn}) C_y(\theta_{ijn}, \phi_{ijn}) d^3 r \\
&- \sqrt{\frac{2}{5}} \int \frac{1}{r r_{ijn}} G_{n^1 \frac{1}{2}}^{a_j}(r) C_s^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] G_{n^1 \frac{3}{2}}^{a_i}(r_{ijn}) C_{3z^2-r^2}(\theta_{ijn}, \phi_{ijn}) d^3 r
\end{aligned} \tag{2.69}$$

Now applying the result of Slater-Koster table [40] to each term of the RHS of Eq. (2.69),

we have

$$\begin{aligned}
& t_{n'1\frac{1}{2},n1\frac{3}{2}}^{a_j a_i}(\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j) \\
&= -\frac{\sqrt{2}}{3} z^2 (pp\sigma)_{(n'1\frac{1}{2},n1\frac{3}{2})}^{L,d,a_j,a_i} - \frac{\sqrt{2}}{3} (1-z^2) (pp\pi)_{(n'1\frac{1}{2},n1\frac{3}{2})}^{L,d,a_j,a_i} + \frac{1}{3\sqrt{2}} x^2 (pp\sigma)_{(n'1\frac{1}{2},n1\frac{3}{2})}^{L,d,a_j,a_i} + \frac{1}{3\sqrt{2}} (1-x^2) \\
&\times (pp\pi)_{(n'1\frac{1}{2},n1\frac{3}{2})}^{L,d,a_j,a_i} + \frac{i}{3\sqrt{2}} \{xy \left[(pp\sigma)_{(n'1\frac{1}{2},n1\frac{3}{2})}^{L,d,a_j,a_i} - (pp\pi)_{(n'1\frac{1}{2},n1\frac{3}{2})}^{L,d,a_j,a_i} \right] - \frac{i}{3\sqrt{2}} xy \left\{ (pp\sigma)_{(n'1\frac{1}{2},n1\frac{3}{2})}^{L,d,a_j,a_i} - \right. \\
&(pp\pi)_{(n'1\frac{1}{2},n1\frac{3}{2})}^{L,d,a_j,a_i} \left. \right\} + \frac{1}{3\sqrt{2}} y^2 (pp\sigma)_{(n'1\frac{1}{2},n1\frac{3}{2})}^{L,d,a_j,a_i} + \frac{1}{3\sqrt{2}} (1-y^2) (pp\pi)_{(n'1\frac{1}{2},n1\frac{3}{2})}^{L,d,a_j,a_i} - \sqrt{\frac{2}{5}} \left\{ z^2 - \frac{1}{2} (x^2 + y^2) \right\} \\
&\times (sd\sigma)_{(n'1\frac{1}{2},n1\frac{3}{2})}^{S,d,a_j,a_i} \\
&= \frac{1}{2} (3z^2 - 1) \left\{ -\frac{\sqrt{2}}{3} (pp\sigma)_{(n'1\frac{1}{2},n1\frac{3}{2})}^{L,d,a_j,a_i} + \frac{\sqrt{2}}{3} (pp\pi)_{(n'1\frac{1}{2},n1\frac{3}{2})}^{L,d,a_j,a_i} - \sqrt{\frac{2}{5}} (sd\sigma)_{(n'1\frac{1}{2},n1\frac{3}{2})}^{S,d,a_j,a_i} \right\} \quad (2.70)
\end{aligned}$$

Comparing Eq. (2.67) and (2.70), we get

$$t_{n'1\frac{1}{2},n1\frac{3}{2}}^{a_j a_i}(\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j) = \frac{1}{2} (3z^2 - 1) K_d^{a_j a_i} \left(n'1\frac{1}{2}, n1\frac{3}{2} \right)_{1/2}. \quad (2.71)$$

(7) Relativistic hopping integral for the combination of $\left(n'1\frac{3}{2} \frac{1}{2} \right)$ and $\left(n0\frac{1}{2} \frac{1}{2} \right)$ atomic orbitals:

From Eq. (2.31), we have

$$\begin{aligned}
& t_{n'1\frac{3}{2},n0\frac{1}{2}}^{a_j a_i}(\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j) \\
&= \sqrt{\frac{2}{3}} \int \frac{1}{r r_{ijn}} F_{n'1\frac{3}{2}}^{a_j}(r) Y_{1,0}^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] F_{n0\frac{1}{2}}^{a_i}(r_{ijn}) Y_{0,0}(\theta_{ijn}, \phi_{ijn}) d^3 r \\
&+ \sqrt{\frac{2}{15}} \int \frac{1}{r r_{ijn}} G_{n'1\frac{3}{2}}^{a_j}(r) Y_{2,0}^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] G_{n0\frac{1}{2}}^{a_i}(r_{ijn}) Y_{1,0}(\theta_{ijn}, \phi_{ijn}) d^3 r
\end{aligned}$$

$$+\sqrt{\frac{2}{5}} \int \frac{1}{r r_{ijn}} G_{n' \frac{3}{2}}^{a_j}(r) Y_{2,1}^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] G_{n0 \frac{1}{2}}^{a_i}(r_{ijn}) Y_{1,1}(\theta_{ijn}, \phi_{ijn}) d^3 r \quad (2.72)$$

According to the definition of relativistic TB parameter [Eq. (2.27)], we have

$$\begin{aligned} & K_d^{a_j a_i} \left(n' 1 \frac{3}{2}, n0 \frac{1}{2} \right)_{1/2} \\ &= \sqrt{\frac{2}{3}} \int \frac{1}{r r_{ijn}} F_{n' \frac{3}{2}}^{a_j}(r) Y_{1,0}^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - |\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j| \mathbf{e}_z)}{2} \right] F_{n0 \frac{1}{2}}^{a_i}(r_{ijn}^z) Y_{0,0}(\theta_{ijn}^z, \phi) d^3 r \\ &+ \sqrt{\frac{2}{15}} \int \frac{1}{r r_{ijn}} G_{n' \frac{3}{2}}^{a_j}(r) Y_{2,0}^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - |\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j| \mathbf{e}_z)}{2} \right] G_{n0 \frac{1}{2}}^{a_i}(r_{ijn}^z) Y_{1,0}(\theta_{ijn}^z, \phi) d^3 r \\ &+ \sqrt{\frac{2}{5}} \int \frac{1}{r r_{ijn}} G_{n' \frac{3}{2}}^{a_j}(r) Y_{2,1}^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - |\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j| \mathbf{e}_z)}{2} \right] G_{n \frac{3}{2}}^{a_i}(r_{ijn}^z) Y_{1,1}(\theta_{ijn}^z, \phi) d^3 r \\ &= \sqrt{\frac{2}{3}} (ps\sigma)_{(n' \frac{3}{2}, n0 \frac{1}{2})}^{L, d, a_j, a_i} + \sqrt{\frac{2}{15}} (dp\sigma)_{(n' \frac{3}{2}, n0 \frac{1}{2})}^{S, d, a_j, a_i} + \sqrt{\frac{2}{5}} (dp\pi)_{(n' \frac{3}{2}, n0 \frac{1}{2})}^{S, d, a_j, a_i} \end{aligned} \quad (2.73)$$

By using cubic harmonics, Eq. (2.72) can be written as

$$\begin{aligned} & t_{n' \frac{3}{2}, n0 \frac{1}{2}}^{a_j a_i}(\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j) \\ &= \sqrt{\frac{2}{3}} \int \frac{1}{r r_{ijn}} F_{n' \frac{3}{2}}^{a_j}(r) C_z^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] F_{n0 \frac{1}{2}}^{a_i}(r_{ijn}) C_s(\theta_{ijn}, \phi_{ijn}) d^3 r \\ &+ \sqrt{\frac{2}{15}} \int \frac{1}{r r_{ijn}} G_{n' \frac{3}{2}}^{a_j}(r) C_{3z^2 - r^2}^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] G_{n0 \frac{1}{2}}^{a_i}(r_{ijn}) C_z(\theta_{ijn}, \phi_{ijn}) d^3 r \\ &+ \sqrt{\frac{2}{5}} \int \frac{1}{r r_{ijn}} G_{n' \frac{3}{2}}^{a_j}(r) \left\{ -\frac{1}{\sqrt{2}} [C_{xz}(\theta, \phi) + iC_{yz}(\theta, \phi)] \right\}^* \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] \\ &\quad \times G_{n0 \frac{1}{2}}^{a_i}(r_{ijn}) \left\{ -\frac{1}{\sqrt{2}} [C_x(\theta_{ijn}, \phi_{ijn}) + iC_y(\theta_{ijn}, \phi_{ijn})] \right\} d^3 r \end{aligned} \quad (2.74)$$

Rearranging Eq. (2.74), we have

$$\begin{aligned}
& t_{n'1\frac{3}{2},n0\frac{1}{2}}^{a_j a_i}(\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j) \\
&= \sqrt{\frac{2}{3}} \int \frac{1}{r r_{ijn}} F_{n'1\frac{3}{2}}^{a_j}(r) C_z^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] F_{n0\frac{1}{2}}^{a_i}(r_{ijn}) C_s(\theta_{ijn}, \phi_{ijn}) d^3 r \\
&+ \sqrt{\frac{2}{15}} \int \frac{1}{r r_{ijn}} G_{n'1\frac{3}{2}}^{a_j}(r) C_{3z^2-r^2}^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] G_{n0\frac{1}{2}}^{a_i}(r_{ijn}) C_z(\theta_{ijn}, \phi_{ijn}) d^3 r \\
&+ \sqrt{\frac{1}{10}} \int \frac{1}{r r_{ijn}} G_{n'1\frac{3}{2}}^{a_j}(r) C_{xz}^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] G_{n0\frac{1}{2}}^{a_i}(r_{ijn}) C_x(\theta_{ijn}, \phi_{ijn}) d^3 r \\
&+ i \sqrt{\frac{1}{10}} \int \frac{1}{r r_{ijn}} G_{n'1\frac{3}{2}}^{a_j}(r) C_{yz}^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] G_{n0\frac{1}{2}}^{a_i}(r_{ijn}) C_x(\theta_{ijn}, \phi_{ijn}) d^3 r \\
&- i \sqrt{\frac{1}{10}} \int \frac{1}{r r_{ijn}} G_{n'1\frac{3}{2}}^{a_j}(r) C_{xz}^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] G_{n0\frac{1}{2}}^{a_i}(r_{ijn}) C_y(\theta_{ijn}, \phi_{ijn}) d^3 r \\
&+ \sqrt{\frac{1}{10}} \int \frac{1}{r r_{ijn}} G_{n'1\frac{3}{2}}^{a_j}(r) C_{yz}^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] G_{n0\frac{1}{2}}^{a_i}(r_{ijn}) C_y(\theta_{ijn}, \phi_{ijn}) d^3 r
\end{aligned} \tag{2.75}$$

Now applying the result of Slater-Koster table [40] to each term of the RHS of Eq. (2.75), we have

$$\begin{aligned}
& t_{n'1\frac{3}{2},n0\frac{1}{2}}^{a_j a_i}(\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j) \\
&= \sqrt{\frac{2}{3}} z (ps\sigma)_{(n'1\frac{3}{2},n0\frac{1}{2})}^{L,d,a_j,a_i} + \sqrt{\frac{2}{15}} \left\{ z \left[z^2 - \frac{1}{2}(x^2 + y^2) \right] (dp\sigma)_{(n'1\frac{3}{2},n0\frac{1}{2})}^{S,d,a_j,a_i} + \sqrt{3} z(x^2 + y^2) (dp\pi)_{(n'1\frac{3}{2},n0\frac{1}{2})}^{S,d,a_j,a_i} \right\} \\
&+ \sqrt{\frac{1}{10}} \left\{ \sqrt{3} x^2 z (dp\sigma)_{(n'1\frac{3}{2},n0\frac{1}{2})}^{S,d,a_j,a_i} + z(1-2x^2) (dp\pi)_{(n'1\frac{3}{2},n0\frac{1}{2})}^{S,d,a_j,a_i} \right\} + i \sqrt{\frac{1}{10}} \left\{ \sqrt{3} xyz (dp\sigma)_{(n'1\frac{3}{2},n0\frac{1}{2})}^{S,d,a_j,a_i} - 2xyz \right. \\
&\times (dp\pi)_{(n'1\frac{3}{2},n0\frac{1}{2})}^{S,d,a_j,a_i} \left. \right\} - i \sqrt{\frac{1}{10}} \left\{ \sqrt{3} xyz (dp\sigma)_{(n'1\frac{3}{2},n0\frac{1}{2})}^{S,d,a_j,a_i} - 2xyz (dp\pi)_{(n'1\frac{3}{2},n0\frac{1}{2})}^{S,d,a_j,a_i} \right\} + \sqrt{\frac{1}{10}} \left\{ \sqrt{3} y^2 z (dp\sigma)_{(n'1\frac{3}{2},n0\frac{1}{2})}^{S,d,a_j,a_i} \right. \\
&+ z(1-2y^2) (dp\pi)_{(n'1\frac{3}{2},n0\frac{1}{2})}^{S,d,a_j,a_i} \left. \right\} \\
&= z \left\{ \sqrt{\frac{2}{3}} (ps\sigma)_{(n'1\frac{3}{2},n0\frac{1}{2})}^{L,d,a_j,a_i} + \sqrt{\frac{2}{15}} (dp\sigma)_{(n'1\frac{3}{2},n0\frac{1}{2})}^{S,d,a_j,a_i} + \sqrt{\frac{2}{5}} (dp\pi)_{(n'1\frac{3}{2},n0\frac{1}{2})}^{S,d,a_j,a_i} \right\}.
\end{aligned} \tag{2.76}$$

Comparing Eqs. (2.73) and (2.76), we get

$$t_{n'1\frac{3}{2},n0\frac{1}{2}}^{a_j a_i}(\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j) = z K_d^{a_j a_i} \left(n'1\frac{3}{2}, n0\frac{1}{2} \right)_{1/2}. \quad (2.77)$$

(8) Relativistic hopping integral for the combination of $\left(n'1\frac{3}{2} \frac{1}{2} \right)$ and $\left(n1\frac{1}{2} \frac{1}{2} \right)$ atomic orbitals:

From Eq. (2.32), we have

$$\begin{aligned} & t_{n'1\frac{3}{2},n1\frac{1}{2}}^{a_j a_i}(\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j) \\ &= -\frac{\sqrt{2}}{3} \int \frac{1}{r r_{ijn}} F_{n'1\frac{3}{2}}^{a_j}(r) Y_{1,0}^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] F_{n1\frac{1}{2}}^{a_i}(r_{ijn}) Y_{1,0}(\theta_{ijn}, \phi_{ijn}) d^3 r \\ &+ \frac{\sqrt{2}}{3} \int \frac{1}{r r_{ijn}} F_{n'1\frac{3}{2}}^{a_j}(r) Y_{1,1}^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] F_{n1\frac{1}{2}}^{a_i}(r_{ijn}) Y_{1,1}(\theta_{ijn}, \phi_{ijn}) d^3 r \\ &+ \sqrt{\frac{2}{5}} \int \frac{1}{r r_{ijn}} G_{n'1\frac{3}{2}}^{a_j}(r) Y_{2,0}^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] G_{n1\frac{1}{2}}^{a_i}(r_{ijn}) Y_{0,0}(\theta_{ijn}, \phi_{ijn}) d^3 r \end{aligned} \quad (2.78)$$

According to the definition of relativistic TB parameter [Eq. (2.27)], we have

$$\begin{aligned} & K_d^{a_j a_i} \left(n'1\frac{3}{2}, n1\frac{1}{2} \right)_{1/2} \\ &= -\frac{\sqrt{2}}{3} \int \frac{1}{r r_{ijn}} F_{n'1\frac{3}{2}}^{a_j}(r) Y_{1,0}^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(|\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j| \mathbf{e}_z)}{2} \right] F_{n1\frac{1}{2}}^{a_i}(r_{ijn}^z) Y_{1,0}(\theta_{ijn}^z, \phi) d^3 r \\ &+ \frac{\sqrt{2}}{3} \int \frac{1}{r r_{ijn}} F_{n'1\frac{3}{2}}^{a_j}(r) Y_{1,1}^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(|\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j| \mathbf{e}_z)}{2} \right] F_{n1\frac{1}{2}}^{a_i}(r_{ijn}^z) Y_{1,1}(\theta_{ijn}^z, \phi) d^3 r \\ &+ \sqrt{\frac{2}{5}} \int \frac{1}{r r_{ijn}} G_{n'1\frac{3}{2}}^{a_j}(r) Y_{2,0}^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(|\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j| \mathbf{e}_z)}{2} \right] G_{n1\frac{1}{2}}^{a_i}(r_{ijn}^z) Y_{0,0}(\theta_{ijn}^z, \phi) d^3 r \end{aligned}$$

$$= -\frac{\sqrt{2}}{3} (pp\sigma)_{(n^1\frac{3}{2}, n^1\frac{1}{2})}^{L,d,a_j,a_i} + \frac{\sqrt{2}}{3} (pp\pi)_{(n^1\frac{3}{2}, n^1\frac{1}{2})}^{L,d,a_j,a_i} - \sqrt{\frac{2}{5}} (ds\sigma)_{(n^1\frac{3}{2}, n^1\frac{1}{2})}^{S,d,a_j,a_i} \quad (2.79)$$

By using cubic harmonics, Eq. (2.78) can be written as

$$\begin{aligned} & t_{n^1\frac{3}{2}, n^1\frac{1}{2}}^{a_j a_i}(\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j) = \\ & -\frac{\sqrt{2}}{3} \int \frac{1}{r r_{ijn}} F_{n^1\frac{3}{2}}^{a_j}(r) C_z^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] F_{n^1\frac{1}{2}}^{a_i}(r_{ijn}) C_z(\theta_{ijn}, \phi_{ijn}) d^3 r \\ & + \frac{\sqrt{2}}{3} \int \frac{1}{r r_{ijn}} F_{n^1\frac{3}{2}}^{a_j}(r) \left\{ -\frac{1}{\sqrt{2}} [C_x(\theta, \phi) + iC_y(\theta, \phi)] \right\}^* \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] \\ & \quad \times F_{n^1\frac{1}{2}}^{a_i}(r_{ijn}) \left\{ -\frac{1}{\sqrt{2}} [C_x(\theta_{ijn}, \phi_{ijn}) + iC_y(\theta_{ijn}, \phi_{ijn})] \right\} d^3 r \\ & - \sqrt{\frac{2}{5}} \int \frac{1}{r r_{ijn}} G_{n^1\frac{3}{2}}^{a_j}(r) C_{3z^2-r^2}^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] G_{n^1\frac{1}{2}}^{a_i}(r_{ijn}) C_s(\theta_{ijn}, \phi_{ijn}) d^3 r \end{aligned} \quad (2.80)$$

Rearranging Eq. (2.80), we have

$$\begin{aligned} & t_{n^1\frac{3}{2}, n^1\frac{1}{2}}^{a_j a_i}(\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j) = \\ & -\frac{\sqrt{2}}{3} \int \frac{1}{r r_{ijn}} F_{n^1\frac{3}{2}}^{a_j}(r) C_z^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] F_{n^1\frac{1}{2}}^{a_i}(r_{ijn}) C_z(\theta_{ijn}, \phi_{ijn}) d^3 r \\ & + \frac{1}{3\sqrt{2}} \int \frac{1}{r r_{ijn}} F_{n^1\frac{3}{2}}^{a_j}(r) C_x^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] F_{n^1\frac{1}{2}}^{a_i}(r_{ijn}) C_x(\theta_{ijn}, \phi_{ijn}) d^3 r \\ & + i \frac{1}{3\sqrt{2}} \int \frac{1}{r r_{ijn}} F_{n^1\frac{3}{2}}^{a_j}(r) C_x^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] F_{n^1\frac{1}{2}}^{a_i}(r_{ijn}) C_y(\theta_{ijn}, \phi_{ijn}) d^3 r \\ & - i \frac{1}{3\sqrt{2}} \int \frac{1}{r r_{ijn}} F_{n^1\frac{3}{2}}^{a_j}(r) C_y^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] F_{n^1\frac{1}{2}}^{a_i}(r_{ijn}) C_x(\theta_{ijn}, \phi_{ijn}) d^3 r \\ & + \frac{1}{3\sqrt{2}} \int \frac{1}{r r_{ijn}} F_{n^1\frac{3}{2}}^{a_j}(r) C_y^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] F_{n^1\frac{1}{2}}^{a_i}(r_{ijn}) C_y(\theta_{ijn}, \phi_{ijn}) d^3 r \end{aligned}$$

$$-\sqrt{\frac{2}{5}} \int \frac{1}{r r_{ijn}} G_{n' \frac{3}{2}}^{a_j}(r) * C_{3z^2-r^2}^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] G_{n' \frac{1}{2}}^{a_i}(r_{ijn}) C_s(\theta_{ijn}, \phi_{ijn}) d^3 r \quad (2.81)$$

Now applying the result of Slater-Koster table [40] to each term of the RHS of Eq. (2.81), we have

$$\begin{aligned} t_{n' \frac{3}{2}, n' \frac{1}{2}}^{a_j a_i}(\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j) = & \\ & -\frac{\sqrt{2}}{3} z^2 (pp\sigma)_{(n' \frac{3}{2}, n' \frac{1}{2})}^{L, d, a_j, a_i} - \frac{\sqrt{2}}{3} (1-z^2) (pp\pi)_{(n' \frac{3}{2}, n' \frac{1}{2})}^{L, d, a_j, a_i} + \frac{1}{3\sqrt{2}} x^2 (pp\sigma)_{(n' \frac{3}{2}, n' \frac{1}{2})}^{L, d, a_j, a_i} + \frac{1}{3\sqrt{2}} (1-x^2) \\ & \times (pp\pi)_{(n' \frac{3}{2}, n' \frac{1}{2})}^{L, d, a_j, a_i} + \frac{i}{3\sqrt{2}} \left\{ xy \left[(pp\sigma)_{(n' \frac{3}{2}, n' \frac{1}{2})}^{L, d, a_j, a_i} - (pp\pi)_{(n' \frac{3}{2}, n' \frac{1}{2})}^{L, d, a_j, a_i} \right] - \frac{i}{3\sqrt{2}} \left\{ xy \left[(pp\sigma)_{(n' \frac{3}{2}, n' \frac{1}{2})}^{L, d, a_j, a_i} - \right. \right. \right. \\ & \left. \left. (pp\pi)_{(n' \frac{3}{2}, n' \frac{1}{2})}^{L, d, a_j, a_i} \right] + \frac{1}{3\sqrt{2}} y^2 (pp\sigma)_{(n' \frac{3}{2}, n' \frac{1}{2})}^{L, d, a_j, a_i} + \frac{1}{3\sqrt{2}} (1-y^2) (pp\pi)_{(n' \frac{3}{2}, n' \frac{1}{2})}^{L, d, a_j, a_i} - \sqrt{\frac{2}{5}} \left\{ z^2 - \frac{1}{2} (x^2 + y^2) \right\} \right. \\ & \left. \times (ds\sigma)_{(n' \frac{3}{2}, n' \frac{1}{2})}^{S, d, a_j, a_i} \right\} \\ = \frac{1}{2} (3z^2 - 1) & \left\{ -\frac{\sqrt{2}}{3} (pp\sigma)_{(n' \frac{3}{2}, n' \frac{1}{2})}^{L, d, a_j, a_i} + \frac{\sqrt{2}}{3} (pp\pi)_{(n' \frac{3}{2}, n' \frac{1}{2})}^{L, d, a_j, a_i} - \sqrt{\frac{2}{5}} (ds\sigma)_{(n' \frac{3}{2}, n' \frac{1}{2})}^{S, d, a_j, a_i} \right\} \quad (2.82) \end{aligned}$$

Comparing Eqs. (2.79) and (2.82), we get

$$t_{n' \frac{3}{2}, n' \frac{1}{2}}^{a_j a_i}(\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j) = \frac{1}{2} (3z^2 - 1) K_d^{a_j a_i} \left(n' \frac{3}{2}, n' \frac{1}{2} \right)_{1/2} \quad (2.83)$$

(9) Relativistic hopping integral for the combination of $\left(n' \frac{3}{2} \frac{1}{2} \right)$ and $\left(n' \frac{3}{2} \frac{1}{2} \right)$ atomic orbitals:

From Eq. (2.31), we have

$$t_{n' \frac{3}{2}, n' \frac{3}{2}}^{a_j a_i}(\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j)$$

$$\begin{aligned}
&= \frac{2}{3} \int \frac{1}{r r_{ijn}} F_{n'1\frac{3}{2}}^{a_j}(r) Y_{1,0}^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] F_{n'1\frac{3}{2}}^{a_i}(r_{ijn}) Y_{1,0}(\theta_{ijn}, \phi_{ijn}) d^3 r \\
&+ \frac{1}{3} \int \frac{1}{r r_{ijn}} F_{n'1\frac{3}{2}}^{a_j}(r) Y_{1,1}^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] F_{n'1\frac{3}{2}}^{a_i}(r_{ijn}) Y_{1,1}(\theta_{ijn}, \phi_{ijn}) d^3 r \\
&+ \frac{2}{5} \int \frac{1}{r r_{ijn}} G_{n'1\frac{3}{2}}^{a_j}(r) Y_{2,0}^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] G_{n'1\frac{3}{2}}^{a_i}(r_{ijn}) Y_{2,0}(\theta_{ijn}, \phi_{ijn}) d^3 r \\
&+ \frac{3}{5} \int \frac{1}{r r_{ijn}} G_{n'1\frac{3}{2}}^{a_j}(r) Y_{2,1}^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] G_{n'1\frac{3}{2}}^{a_i}(r_{ijn}) Y_{2,1}(\theta_{ijn}, \phi_{ijn}) d^3 r \quad (2.84)
\end{aligned}$$

According to the definition of relativistic TB parameter [Eq. (2.27)], we have

$$\begin{aligned}
&K_d^{a_j a_i} \left(n'1\frac{3}{2}, n1\frac{3}{2} \right)_{1/2} \\
&= \frac{2}{3} \int \frac{1}{r r_{ijn}} F_{n'1\frac{3}{2}}^{a_j}(r) Y_{1,0}^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(|\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j| \mathbf{e}_z)}{2} \right] F_{n'1\frac{3}{2}}^{a_i}(r_{ijn}^z) Y_{1,0}(\theta_{ijn}^z, \phi) d^3 r \\
&+ \frac{1}{3} \int \frac{1}{r r_{ijn}} F_{n'1\frac{3}{2}}^{a_j}(r) Y_{1,1}^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(|\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j| \mathbf{e}_z)}{2} \right] F_{n'1\frac{3}{2}}^{a_i}(r_{ijn}^z) Y_{1,1}(\theta_{ijn}^z, \phi) d^3 r \\
&+ \frac{2}{5} \int \frac{1}{r r_{ijn}} G_{n'1\frac{3}{2}}^{a_j}(r) Y_{2,0}^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(|\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j| \mathbf{e}_z)}{2} \right] G_{n'1\frac{3}{2}}^{a_i}(r_{ijn}^z) Y_{2,0}(\theta_{ijn}^z, \phi) d^3 r \\
&+ \frac{3}{5} \int \frac{1}{r r_{ijn}} G_{n'1\frac{3}{2}}^{a_j}(r) Y_{2,1}^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(|\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j| \mathbf{e}_z)}{2} \right] G_{n'1\frac{3}{2}}^{a_i}(r_{ijn}^z) Y_{2,1}(\theta_{ijn}^z, \phi) d^3 r \\
&= \frac{2}{3} (pp\sigma)_{(n'1\frac{3}{2}, n1\frac{3}{2})}^{L,d,a_j,a_i} + \frac{1}{3} (pp\pi)_{(n'1\frac{3}{2}, n1\frac{3}{2})}^{L,d,a_j,a_i} + \frac{2}{5} (dd\sigma)_{(n'1\frac{3}{2}, n1\frac{3}{2})}^{S,d,a_j,a_i} + \frac{3}{5} (dd\pi)_{(n'1\frac{3}{2}, n1\frac{3}{2})}^{S,d,a_j,a_i} \quad (2.85)
\end{aligned}$$

Applying cubic harmonics, Eq. (2.84) can be written as

$$\begin{aligned}
&t_{n'1\frac{3}{2}, n1\frac{3}{2}}^{a_j a_i}(\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j) \\
&= \frac{2}{3} \int \frac{1}{r r_{ijn}} F_{n'1\frac{3}{2}}^{a_j}(r) C_z^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] F_{n'1\frac{3}{2}}^{a_i}(r_{ijn}) C_z(\theta_{ijn}, \phi_{ijn}) d^3 r
\end{aligned}$$

$$\begin{aligned}
& + \frac{1}{3} \int \frac{1}{r r_{ijn}} F_{n'1\frac{3}{2}}^{a_j}(r)^* \left\{ -\frac{1}{\sqrt{2}} [C_x(\theta, \phi) + iC_y(\theta, \phi)] \right\}^* \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] \\
& \quad \times F_{n1\frac{3}{2}}^{a_i}(r_{ijn}) \left\{ -\frac{1}{\sqrt{2}} [C_x(\theta_{ijn}, \phi_{ijn}) + iC_y(\theta_{ijn}, \phi_{ijn})] \right\} d^3 r \\
& + \frac{2}{5} \int \frac{1}{r r_{ijn}} G_{n'1\frac{3}{2}}^{a_j}(r)^* C_{3z^2-r^2}^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] G_{n1\frac{3}{2}}^{a_i}(r_{ijn}) C_{3z^2-r^2}(\theta_{ijn}, \phi_{ijn}) d^3 r \\
& + \frac{3}{5} \int \frac{1}{r r_{ijn}} G_{n'1\frac{3}{2}}^{a_j}(r)^* \left\{ -\frac{1}{\sqrt{2}} [C_{xz}(\theta, \phi) + iC_{yz}(\theta, \phi)] \right\}^* \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] \\
& \quad \times G_{n1\frac{3}{2}}^{a_i}(r_{ijn}) \left\{ -\frac{1}{\sqrt{2}} [C_{xz}(\theta_{ijn}, \phi_{ijn}) + iC_{yz}(\theta_{ijn}, \phi_{ijn})] \right\} d^3 r \tag{2.86}
\end{aligned}$$

Rearranging Eq. (2.86), we have

$$\begin{aligned}
& t_{n'1\frac{3}{2}, n1\frac{3}{2}}^{a_j a_i}(\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j) \\
& = \frac{2}{3} \int \frac{1}{r r_{ijn}} F_{n'1\frac{3}{2}}^{a_j}(r)^* C_z^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] F_{n1\frac{3}{2}}^{a_i}(r_{ijn}) C_z(\theta_{ijn}, \phi_{ijn}) d^3 r \\
& + \frac{1}{6} \int \frac{1}{r r_{ijn}} F_{n'1\frac{3}{2}}^{a_j}(r)^* C_x^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] F_{n1\frac{3}{2}}^{a_i}(r_{ijn}) C_x(\theta_{ijn}, \phi_{ijn}) d^3 r \\
& + i \frac{1}{6} \int \frac{1}{r r_{ijn}} F_{n'1\frac{3}{2}}^{a_j}(r)^* C_x^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] F_{n1\frac{3}{2}}^{a_i}(r_{ijn}) C_y(\theta_{ijn}, \phi_{ijn}) d^3 r \\
& - i \frac{1}{6} \int \frac{1}{r r_{ijn}} F_{n'1\frac{3}{2}}^{a_j}(r)^* C_y^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] F_{n1\frac{3}{2}}^{a_i}(r_{ijn}) C_x(\theta_{ijn}, \phi_{ijn}) d^3 r \\
& + \frac{1}{6} \int \frac{1}{r r_{ijn}} F_{n'1\frac{3}{2}}^{a_j}(r)^* C_y^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] F_{n1\frac{3}{2}}^{a_i}(r_{ijn}) C_y(\theta_{ijn}, \phi_{ijn}) d^3 r \\
& + \frac{2}{5} \int \frac{1}{r r_{ijn}} G_{n'1\frac{3}{2}}^{a_j}(r)^* C_{3z^2-r^2}^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] G_{n1\frac{3}{2}}^{a_i}(r_{ijn}) C_{3z^2-r^2}(\theta_{ijn}, \phi_{ijn}) d^3 r \\
& + \frac{3}{10} \int \frac{1}{r r_{ijn}} G_{n'1\frac{3}{2}}^{a_j}(r)^* C_{xz}^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] G_{n1\frac{3}{2}}^{a_i}(r_{ijn}) C_{xz}(\theta_{ijn}, \phi_{ijn}) d^3 r
\end{aligned}$$

$$\begin{aligned}
& +i \frac{3}{10} \int \frac{1}{r r_{ijn}} G_{n1\frac{3}{2}}^{a_j}(\mathbf{r})^* C_{xz}(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] G_{n1\frac{3}{2}}^{a_i}(r_{ijn}) C_{yz}(\theta_{ijn}, \phi_{ijn}) d^3 r \\
& -i \frac{3}{10} \int \frac{1}{r r_{ijn}} G_{n1\frac{3}{2}}^{a_j}(\mathbf{r})^* C_{yz}(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] G_{n1\frac{3}{2}}^{a_i}(r_{ijn}) C_{xz}(\theta_{ijn}, \phi_{ijn}) d^3 r \\
& + \frac{3}{10} \int \frac{1}{r r_{ijn}} G_{n1\frac{3}{2}}^{a_j}(\mathbf{r})^* C_{yz}(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] G_{n1\frac{3}{2}}^{a_i}(r_{ijn}) C_{yz}(\theta_{ijn}, \phi_{ijn}) d^3 r \quad (2.87)
\end{aligned}$$

Now applying the result of Slater-Koster table [40] to each term of the RHS of Eq. (2.87), we have

$$\begin{aligned}
& t_{n1\frac{3}{2}, n1\frac{3}{2}}^{a_j a_i}(\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j) \\
& = \frac{2}{3} z^2 (pp\sigma)_{(n1\frac{3}{2}, n1\frac{3}{2})}^{L, d, a_j, a_i} + \frac{2}{3} (1 - z^2) (pp\pi)_{(n1\frac{3}{2}, n1\frac{3}{2})}^{L, d, a_j, a_i} + \frac{1}{6} x^2 (pp\sigma)_{(n1\frac{3}{2}, n1\frac{3}{2})}^{L, d, a_j, a_i} + \frac{1}{6} (1 - x^2) (pp\pi)_{(n1\frac{3}{2}, n1\frac{3}{2})}^{L, d, a_j, a_i} \\
& + \frac{i}{6} \left\{ xy \left[(pp\sigma)_{(n1\frac{3}{2}, n1\frac{3}{2})}^{L, d, a_j, a_i} - (pp\pi)_{(n1\frac{3}{2}, n1\frac{3}{2})}^{L, d, a_j, a_i} \right] - \frac{i}{6} \left\{ xy \left[(pp\sigma)_{(n1\frac{3}{2}, n1\frac{3}{2})}^{L, d, a_j, a_i} - (pp\pi)_{(n1\frac{3}{2}, n1\frac{3}{2})}^{L, d, a_j, a_i} \right] + \frac{1}{6} y^2 \right. \right. \\
& \times (pp\sigma)_{(n1\frac{3}{2}, n1\frac{3}{2})}^{L, d, a_j, a_i} + \frac{1}{6} (1 - y^2) (pp\pi)_{(n1\frac{3}{2}, n1\frac{3}{2})}^{L, d, a_j, a_i} + \frac{2}{5} \left[\left\{ z^2 - \frac{1}{2} (x^2 + y^2) \right\} (dd\sigma)_{(n1\frac{3}{2}, n1\frac{3}{2})}^{S, d, a_j, a_i} + 3z^2 (x^2 + y^2) \right. \\
& \times (dd\pi)_{(n1\frac{3}{2}, n1\frac{3}{2})}^{S, d, a_j, a_i} + \frac{3}{4} (x^2 + y^2)^2 (dd\delta)_{(n1\frac{3}{2}, n1\frac{3}{2})}^{S, d, a_j, a_i} \left. \right] + \frac{3}{10} [3x^2 z^2 (dd\sigma)_{(n1\frac{3}{2}, n1\frac{3}{2})}^{S, d, a_j, a_i} + (x^2 + z^2 - 4x^2 z^2) \\
& \times (dd\pi)_{(n1\frac{3}{2}, n1\frac{3}{2})}^{S, d, a_j, a_i} + (y^2 + x^2 z^2) (dd\delta)_{(n1\frac{3}{2}, n1\frac{3}{2})}^{S, d, a_j, a_i} \left. \right] + i \frac{3}{10} [3xz^2 y (dd\sigma)_{(n1\frac{3}{2}, n1\frac{3}{2})}^{S, d, a_j, a_i} + xy(1 - 4z^2) (dd\pi)_{(n1\frac{3}{2}, n1\frac{3}{2})}^{S, d, a_j, a_i} \\
& + xy(z^2 - 1) (dd\delta)_{(n1\frac{3}{2}, n1\frac{3}{2})}^{S, d, a_j, a_i} \left. \right] - i \frac{3}{10} [3xz^2 y (dd\sigma)_{(n1\frac{3}{2}, n1\frac{3}{2})}^{S, d, a_j, a_i} + xy(1 - 4z^2) (dd\pi)_{(n1\frac{3}{2}, n1\frac{3}{2})}^{S, d, a_j, a_i} + xy(z^2 - 1) \\
& \times (dd\delta)_{(n1\frac{3}{2}, n1\frac{3}{2})}^{S, d, a_j, a_i} \left. \right] + \frac{3}{10} [3y^2 z^2 (dd\sigma)_{(n1\frac{3}{2}, n1\frac{3}{2})}^{S, d, a_j, a_i} + (y^2 + z^2 - 4y^2 z^2) (dd\pi)_{(n1\frac{3}{2}, n1\frac{3}{2})}^{S, d, a_j, a_i} + (x^2 + y^2 z^2) \\
& \times (dd\delta)_{(n1\frac{3}{2}, n1\frac{3}{2})}^{S, d, a_j, a_i} \left. \right] \\
& = \frac{1}{4} (1 + 3z^2) \left\{ \frac{2}{3} (pp\sigma)_{(n1\frac{3}{2}, n1\frac{3}{2})}^{L, d, a_j, a_i} + \frac{1}{3} (pp\pi)_{(n1\frac{3}{2}, n1\frac{3}{2})}^{L, d, a_j, a_i} + \frac{2}{5} (dd\sigma)_{(n1\frac{3}{2}, n1\frac{3}{2})}^{S, d, a_j, a_i} + \frac{3}{5} (dd\pi)_{(n1\frac{3}{2}, n1\frac{3}{2})}^{S, d, a_j, a_i} + \frac{3}{4} (1 - z^2) \right.
\end{aligned}$$

$$\times \left\{ (pp\pi)_{(n'1\frac{3}{2}, n1\frac{3}{2})}^{S,d,a_j,a_i} + \frac{1}{5} (dd\pi)_{(n'1\frac{3}{2}, n1\frac{3}{2})}^{S,d,a_j,a_i} + \frac{4}{5} (dd\delta)_{(n'1\frac{3}{2}, n1\frac{3}{2})}^{S,d,a_j,a_i} \right\} \quad (2.88)$$

From Eqs. (2.85), (2.91) and (2.88), we get

$$t_{n'1\frac{3}{2}, n1\frac{3}{2}}^{a_j a_i}(\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j) = \frac{1}{4} (1 + 3z^2) K_d^{a_j a_i} \frac{\mathfrak{E}}{\mathfrak{E}} n \mathfrak{C} 1 \frac{3}{2}, n1 \frac{3\ddot{0}}{2\ddot{0}_{1/2}} + \frac{3}{4} (1 - z^2) K_d^{a_j a_i} \frac{\mathfrak{E}}{\mathfrak{E}} n \mathfrak{C} 1 \frac{3}{2}, n1 \frac{3\ddot{0}}{2\ddot{0}_{3/2}} \quad (2.89)$$

(10) Relativistic hopping integral for the combination of $\left(n'1\frac{3}{2}, \frac{3}{2}\right)$ and $\left(n1\frac{3}{2}, \frac{3}{2}\right)$ atomic orbitals:

From Eq. (2.31), we have

$$\begin{aligned} & t_{n'1\frac{3}{2}, n1\frac{3}{2}}^{a_j a_i}(\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j) \\ &= \int \frac{1}{r r_{ijn}} F_{n'1\frac{3}{2}}^{a_j}(r) Y_{1,1}^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] F_{n1\frac{3}{2}}^{a_i}(r_{ijn}) Y_{1,1}(\theta_{ijn}, \phi_{ijn}) d^3 r \\ &+ \frac{1}{5} \int \frac{1}{r r_{ijn}} G_{n'1\frac{3}{2}}^{a_j}(r) Y_{2,1}^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] G_{n1\frac{3}{2}}^{a_i}(r_{ijn}) Y_{2,1}(\theta_{ijn}, \phi_{ijn}) d^3 r \\ &+ \frac{4}{5} \int \frac{1}{r r_{ijn}} G_{n'1\frac{3}{2}}^{a_j}(r) Y_{2,2}^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] G_{n1\frac{3}{2}}^{a_i}(r_{ijn}) Y_{2,2}(\theta_{ijn}, \phi_{ijn}) d^3 r \quad (2.90) \end{aligned}$$

According to the definition of relativistic TB parameter [Eq. (2.27)], we have

$$\begin{aligned} & K_d^{a_j a_i} \left(n'1\frac{3}{2}, n1\frac{3}{2} \right)_{3/2} \\ &= \int \frac{1}{r r_{ijn}} F_{n'1\frac{3}{2}}^{a_j}(r) Y_{1,1}^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(|\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j| \mathbf{e}_z)}{2} \right] F_{n1\frac{3}{2}}^{a_i}(r_{ijn}^z) Y_{1,1}(\theta_{ijn}^z, \phi) d^3 r \\ &+ \frac{1}{5} \int \frac{1}{r r_{ijn}} G_{n'1\frac{3}{2}}^{a_j}(r) Y_{2,1}^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(|\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j| \mathbf{e}_z)}{2} \right] G_{n1\frac{3}{2}}^{a_i}(r_{ijn}^z) Y_{2,1}(\theta_{ijn}^z, \phi) d^3 r \end{aligned}$$

$$\begin{aligned}
& + \frac{4}{5} \int \frac{1}{r r_{ijn}} G_{n' \frac{3}{2}}^{a_j}(r) Y_{2,2}^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(|\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j| \mathbf{e}_z)}{2} \right] G_{n' \frac{3}{2}}^{a_i}(r_{ijn}^z) Y_{2,2}(\theta_{ijn}^z, \phi) d^3 r \\
& = (pp\pi)_{(n' \frac{3}{2}, n' \frac{3}{2})}^{L,d,a_j,a_i} + \frac{1}{5} (dd\pi)_{(n' \frac{3}{2}, n' \frac{3}{2})}^{S,d,a_j,a_i} + \frac{4}{5} (dd\delta)_{(n' \frac{3}{2}, n' \frac{3}{2})}^{S,d,a_j,a_i} \tag{2.91}
\end{aligned}$$

Using cubic harmonics, Eq. (2.90) can be written as

$$\begin{aligned}
& t_{n' \frac{3}{2}, n' \frac{3}{2}}^{a_j a_i}(\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j) \\
& = \int \frac{1}{r r_{ijn}} F_{n' \frac{3}{2}}^{a_j}(r) \left\{ -\frac{1}{\sqrt{2}} [C_x(\theta, \phi) + iC_y(\theta, \phi)] \right\}^* \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] \\
& \quad \times F_{n' \frac{3}{2}}^{a_i}(r_{ijn}) \left\{ -\frac{1}{\sqrt{2}} [C_x(\theta_{ijn}, \phi_{ijn}) + iC_y(\theta_{ijn}, \phi_{ijn})] \right\} d^3 r \\
& + \frac{1}{5} \int \frac{1}{r r_{ijn}} G_{n' \frac{3}{2}}^{a_j}(r) \left\{ -\frac{1}{\sqrt{2}} [C_{xz}(\theta, \phi) + iC_{yz}(\theta, \phi)] \right\}^* \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] \\
& \quad \times G_{n' \frac{3}{2}}^{a_i}(r_{ijn}) \left\{ -\frac{1}{\sqrt{2}} [C_{xz}(\theta_{ijn}, \phi_{ijn}) + iC_{yz}(\theta_{ijn}, \phi_{ijn})] \right\} d^3 r \\
& + \frac{4}{5} \int \frac{1}{r r_{ijn}} G_{n' \frac{3}{2}}^{a_j}(r) \left\{ \frac{1}{\sqrt{2}} [C_{x^2-y^2}(\theta, \phi) + iC_{xy}(\theta, \phi)] \right\}^* \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] \\
& \quad \times G_{n' \frac{3}{2}}^{a_i}(r_{ijn}) \left\{ \frac{1}{\sqrt{2}} [C_{x^2-y^2}(\theta_{ijn}, \phi_{ijn}) + iC_{xy}(\theta_{ijn}, \phi_{ijn})] \right\} d^3 r \tag{2.92}
\end{aligned}$$

Rearranging Eq. (2.92), we have

$$\begin{aligned}
& t_{n' \frac{3}{2}, n' \frac{3}{2}}^{a_j a_i}(\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j) \\
& = \frac{1}{2} \int \frac{1}{r r_{ijn}} F_{n' \frac{3}{2}}^{a_j}(r) C_x^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] F_{n' \frac{3}{2}}^{a_i}(r_{ijn}) C_x(\theta_{ijn}, \phi_{ijn}) d^3 r \\
& + i \frac{1}{2} \int \frac{1}{r r_{ijn}} F_{n' \frac{3}{2}}^{a_j}(r) C_x^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] F_{n' \frac{3}{2}}^{a_i}(r_{ijn}) C_y(\theta_{ijn}, \phi_{ijn}) d^3 r
\end{aligned}$$

$$\begin{aligned}
& -i \frac{1}{2} \int \frac{1}{r r_{ijn}} F_{n' \frac{1}{2}}^{a_j}(\mathbf{r})^* C_y^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] F_{n' \frac{1}{2}}^{a_i}(r_{ijn}) C_x(\theta_{ijn}, \phi_{ijn}) d^3 r \\
& + \frac{1}{2} \int \frac{1}{r r_{ijn}} F_{n' \frac{1}{2}}^{a_j}(\mathbf{r})^* C_y^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] F_{n' \frac{1}{2}}^{a_i}(r_{ijn}) C_y(\theta_{ijn}, \phi_{ijn}) d^3 r \\
& + \frac{1}{10} \int \frac{1}{r r_{ijn}} G_{n' \frac{1}{2}}^{a_j}(\mathbf{r})^* C_{xz}^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] G_{n' \frac{1}{2}}^{a_i}(r_{ijn}) C_{xz}(\theta_{ijn}, \phi_{ijn}) d^3 r \\
& + i \frac{1}{10} \int \frac{1}{r r_{ijn}} G_{n' \frac{1}{2}}^{a_j}(\mathbf{r})^* C_{xz}^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] G_{n' \frac{1}{2}}^{a_i}(r_{ijn}) C_{yz}(\theta_{ijn}, \phi_{ijn}) d^3 r \\
& - i \frac{1}{10} \int \frac{1}{r r_{ijn}} G_{n' \frac{1}{2}}^{a_j}(\mathbf{r})^* C_{yz}^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] G_{n' \frac{1}{2}}^{a_i}(r_{ijn}) C_{xz}(\theta_{ijn}, \phi_{ijn}) d^3 r \\
& + i \frac{4}{10} \int \frac{1}{r r_{ijn}} G_{n' \frac{1}{2}}^{a_j}(\mathbf{r})^* C_{x^2-y^2}^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] G_{n' \frac{1}{2}}^{a_i}(r_{ijn}) C_{xy}(\theta_{ijn}, \phi_{ijn}) d^3 r \\
& - i \frac{4}{10} \int \frac{1}{r r_{ijn}} G_{n' \frac{1}{2}}^{a_j}(\mathbf{r})^* C_{xy}^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] G_{n' \frac{1}{2}}^{a_i}(r_{ijn}) C_{x^2-y^2}(\theta_{ijn}, \phi_{ijn}) d^3 r \\
& + \frac{4}{10} \int \frac{1}{r r_{ijn}} G_{n' \frac{1}{2}}^{a_j}(\mathbf{r})^* C_{xy}^*(\theta, \phi) \left[\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right] G_{n' \frac{1}{2}}^{a_i}(r_{ijn}) C_{xy}(\theta_{ijn}, \phi_{ijn}) d^3 r \quad (2.93)
\end{aligned}$$

Now applying the result of Slater-Koster table [40] to each term of the RHS of Eq. (2.93), we have

$$\begin{aligned}
& t_{n' \frac{1}{2}, n' \frac{1}{2}}^{a_j a_i}(\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j) \\
& = \frac{1}{2} x^2 (pp\sigma)_{(n' \frac{1}{2}, n' \frac{1}{2})}^{L, d, a_j, a_i} + \frac{1}{2} (1-x^2) (pp\pi)_{(n' \frac{1}{2}, n' \frac{1}{2})}^{L, d, a_j, a_i} + \frac{i}{2} [xy \left\{ (pp\sigma)_{(n' \frac{1}{2}, n' \frac{1}{2})}^{L, d, a_j, a_i} - (pp\pi)_{(n' \frac{1}{2}, n' \frac{1}{2})}^{L, d, a_j, a_i} \right\}] \\
& - \frac{i}{2} [xy \left\{ (pp\sigma)_{(n' \frac{1}{2}, n' \frac{1}{2})}^{L, d, a_j, a_i} - (pp\pi)_{(n' \frac{1}{2}, n' \frac{1}{2})}^{L, d, a_j, a_i} \right\}] + \frac{1}{2} y^2 (pp\sigma)_{(n' \frac{1}{2}, n' \frac{1}{2})}^{L, d, a_j, a_i} + \frac{1}{2} (1-y^2) (pp\pi)_{(n' \frac{1}{2}, n' \frac{1}{2})}^{L, d, a_j, a_i} \\
& + \frac{1}{10} \left\{ 3x^2 z^2 (dd\sigma)_{(n' \frac{1}{2}, n' \frac{1}{2})}^{S, d, a_j, a_i} + (x^2 + z^2 - 4x^2 z^2) (dd\pi)_{(n' \frac{1}{2}, n' \frac{1}{2})}^{S, d, a_j, a_i} + (y^2 + x^2 z^2) (dd\delta)_{(n' \frac{1}{2}, n' \frac{1}{2})}^{S, d, a_j, a_i} \right\} \\
& + \frac{i}{10} \left\{ 3xz^2 y (dd\sigma)_{(n' \frac{1}{2}, n' \frac{1}{2})}^{S, d, a_j, a_i} + xy(1-4z^2) (dd\pi)_{(n' \frac{1}{2}, n' \frac{1}{2})}^{S, d, a_j, a_i} + xy(z^2-1) (dd\delta)_{(n' \frac{1}{2}, n' \frac{1}{2})}^{S, d, a_j, a_i} \right\}
\end{aligned}$$

$$\begin{aligned}
& -\frac{i}{10} \left\{ 3xz^2 y (dd\sigma)_{(n'1\frac{3}{2}, n1\frac{3}{2})}^{S,d,a_j,a_i} + xy(1-4z^2) (dd\pi)_{(n'1\frac{3}{2}, n1\frac{3}{2})}^{S,d,a_j,a_i} + xy(z^2-1) (dd\delta)_{(n'1\frac{3}{2}, n1\frac{3}{2})}^{S,d,a_j,a_i} \right\} \\
& + \frac{1}{10} \left\{ 3y^2 z^2 (dd\sigma)_{(n'1\frac{3}{2}, n1\frac{3}{2})}^{S,d,a_j,a_i} + (y^2+z^2-4y^2 z^2) (dd\pi)_{(n'1\frac{3}{2}, n1\frac{3}{2})}^{S,d,a_j,a_i} + (x^2+y^2 z^2) (dd\delta)_{(n'1\frac{3}{2}, n1\frac{3}{2})}^{S,d,a_j,a_i} \right\} \\
& + \frac{4}{10} \left[\frac{3}{4} (x^2-y^2)^2 (dd\sigma)_{(n'1\frac{3}{2}, n1\frac{3}{2})}^{S,d,a_j,a_i} + \{x^2+y^2-(x^2-y^2)^2\} (dd\pi)_{(n'1\frac{3}{2}, n1\frac{3}{2})}^{S,d,a_j,a_i} + \left\{ z^2 + \frac{1}{4} (x^2-y^2)^2 \right\} \right. \\
& \times (dd\delta)_{(n'1\frac{3}{2}, n1\frac{3}{2})}^{S,d,a_j,a_i} + i \frac{4}{10} \left[\frac{3}{2} xy(x^2-y^2) (dd\sigma)_{(n'1\frac{3}{2}, n1\frac{3}{2})}^{S,d,a_j,a_i} + 2xy(y^2-x^2) (dd\pi)_{(n'1\frac{3}{2}, n1\frac{3}{2})}^{S,d,a_j,a_i} + \frac{1}{2} xy(x^2-y^2) \right. \\
& \times (dd\delta)_{(n'1\frac{3}{2}, n1\frac{3}{2})}^{S,d,a_j,a_i} \left. \right] - i \frac{4}{10} \left[\frac{3}{2} xy(x^2-y^2) (dd\sigma)_{(n'1\frac{3}{2}, n1\frac{3}{2})}^{S,d,a_j,a_i} + 2xy(y^2-x^2) (dd\pi)_{(n'1\frac{3}{2}, n1\frac{3}{2})}^{S,d,a_j,a_i} + \frac{1}{2} xy(x^2-y^2) \right. \\
& \times (dd\delta)_{(n'1\frac{3}{2}, n1\frac{3}{2})}^{S,d,a_j,a_i} \left. \right] + \frac{4}{10} \left[3x^2 y^2 (dd\sigma)_{(n'1\frac{3}{2}, n1\frac{3}{2})}^{S,d,a_j,a_i} + (x^2+y^2-4x^2 y^2) (dd\pi)_{(n'1\frac{3}{2}, n1\frac{3}{2})}^{S,d,a_j,a_i} + (z^2+x^2 y^2) \right. \\
& \times (dd\delta)_{(n'1\frac{3}{2}, n1\frac{3}{2})}^{S,d,a_j,a_i} \left. \right] \\
& = \frac{3}{4} (1-z^2) \left\{ \frac{2}{3} (pp\sigma)_{(n'1\frac{3}{2}, n1\frac{3}{2})}^{L,d,a_j,a_i} + \frac{1}{3} (pp\pi)_{(n'1\frac{3}{2}, n1\frac{3}{2})}^{L,d,a_j,a_i} + \frac{2}{5} (dd\sigma)_{(n'1\frac{3}{2}, n1\frac{3}{2})}^{S,d,a_j,a_i} + \frac{3}{5} (dd\pi)_{(n'1\frac{3}{2}, n1\frac{3}{2})}^{S,d,a_j,a_i} \right\} + \frac{1}{4} (1+3z^2) \\
& \times \left\{ (pp\pi)_{(n'1\frac{3}{2}, n1\frac{3}{2})}^{S,d,a_j,a_i} + \frac{1}{5} (dd\pi)_{(n'1\frac{3}{2}, n1\frac{3}{2})}^{S,d,a_j,a_i} + \frac{4}{5} (dd\delta)_{(n'1\frac{3}{2}, n1\frac{3}{2})}^{S,d,a_j,a_i} \right\} \tag{2.94}
\end{aligned}$$

From Eqs. (2.85), (2.91) and (2.94), we get

$$t_{n'1\frac{3}{2}, n1\frac{3}{2}}^{a_j, a_i} (\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j) = \frac{3}{4} (1-z^2) K_d^{a_j, a_i} \left(n'1\frac{3}{2}, n1\frac{3}{2} \right)_{1/2} + \frac{1}{4} (1+3z^2) K_d^{a_j, a_i} \left(n'1\frac{3}{2}, n1\frac{3}{2} \right)_{3/2}. \tag{2.95}$$

Similarly we can obtain the remaining relations between relativistic TB parameters and relativistic hopping integrals. The results are summarized in Table-I. This table is recognized as the relativistic version of the Slater-koster table, and referred to as the relativistic Slater-Koster table.

Table-I. Relativistic Slater-Koster table

Here x , y , and z denote the direction cosines of $(\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j)$.

$(n\ell, \ell\ell, J\ell, M\ell)$	(n, ℓ, J, M)	Hopping integrals $t_{n\ell JM\ell, n\ell JM}^{a_j a_i}(\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j)$
$\frac{x}{\epsilon} n\ell, 0, \frac{1}{2}, \frac{1\ 0}{2\ 0}$	$\frac{x}{\epsilon} n, 0, \frac{1}{2}, \frac{1\ 0}{2\ 0}$	$K_d^{a_j a_i} \frac{x}{\epsilon} n\ell 0, \frac{1}{2}, n 0 \frac{1\ 0}{2\ 0_{1/2}}$
$\frac{x}{\epsilon} n\ell, 0, \frac{1}{2}, \frac{1\ 0}{2\ 0}$	$\frac{x}{\epsilon} n, 0, \frac{1}{2}, -\frac{1\ 0}{2\ 0}$	0
$\frac{x}{\epsilon} n\ell, 0, \frac{1}{2}, \frac{1\ 0}{2\ 0}$	$\frac{x}{\epsilon} n, 1, \frac{1}{2}, \frac{1\ 0}{2\ 0}$	$z K_d^{a_j a_i} \frac{x}{\epsilon} n\ell 0, \frac{1}{2}, n 1 \frac{1\ 0}{2\ 0_{1/2}}$
$\frac{x}{\epsilon} n\ell, 0, \frac{1}{2}, \frac{1\ 0}{2\ 0}$	$\frac{x}{\epsilon} n, 1, \frac{1}{2}, -\frac{1\ 0}{2\ 0}$	$(x - iy) K_d^{a_j a_i} \frac{x}{\epsilon} n\ell 0, \frac{1}{2}, n 1 \frac{1\ 0}{2\ 0_{1/2}}$
$\frac{x}{\epsilon} n\ell, 0, \frac{1}{2}, \frac{1\ 0}{2\ 0}$	$\frac{x}{\epsilon} n, 1, \frac{3}{2}, \frac{3\ 0}{2\ 0}$	$-\frac{\sqrt{3}}{2} (x + iy) K_d^{a_j a_i} \frac{x}{\epsilon} n\ell 0, \frac{1}{2}, n 1 \frac{3\ 0}{2\ 0_{1/2}}$
$\frac{x}{\epsilon} n\ell, 0, \frac{1}{2}, \frac{1\ 0}{2\ 0}$	$\frac{x}{\epsilon} n, 1, \frac{3}{2}, \frac{1\ 0}{2\ 0}$	$z K_d^{a_j a_i} \frac{x}{\epsilon} n\ell 0, \frac{1}{2}, n 1 \frac{3\ 0}{2\ 0_{1/2}}$
$\frac{x}{\epsilon} n\ell, 0, \frac{1}{2}, \frac{1\ 0}{2\ 0}$	$\frac{x}{\epsilon} n, 1, \frac{3}{2}, -\frac{1\ 0}{2\ 0}$	$\frac{1}{2} (x - iy) K_d^{a_j a_i} \frac{x}{\epsilon} n\ell 0, \frac{1}{2}, n 1 \frac{3\ 0}{2\ 0_{1/2}}$
$\frac{x}{\epsilon} n\ell, 0, \frac{1}{2}, \frac{1\ 0}{2\ 0}$	$\frac{x}{\epsilon} n, 1, \frac{3}{2}, -\frac{3\ 0}{2\ 0}$	0
$\frac{x}{\epsilon} n\ell, 0, \frac{1}{2}, -\frac{1\ 0}{2\ 0}$	$\frac{x}{\epsilon} n, 0, \frac{1}{2}, \frac{1\ 0}{2\ 0}$	0
$\frac{x}{\epsilon} n\ell, 0, \frac{1}{2}, -\frac{1\ 0}{2\ 0}$	$\frac{x}{\epsilon} n, 0, \frac{1}{2}, -\frac{1\ 0}{2\ 0}$	$K_d^{a_j a_i} \frac{x}{\epsilon} n\ell 0, \frac{1}{2}, n 0 \frac{1\ 0}{2\ 0_{1/2}}$
$\frac{x}{\epsilon} n\ell, 0, \frac{1}{2}, -\frac{1\ 0}{2\ 0}$	$\frac{x}{\epsilon} n, 1, \frac{1}{2}, \frac{1\ 0}{2\ 0}$	$(x + iy) K_d^{a_j a_i} \frac{x}{\epsilon} n\ell 0, \frac{1}{2}, n 1 \frac{1\ 0}{2\ 0_{1/2}}$

$\mathfrak{C}_{\mathfrak{e}}^{n\ell, 0, \frac{1}{2}, -\frac{1\ddot{0}}{2\ddot{\theta}}}$	$\mathfrak{C}_{\mathfrak{e}}^{n, 1, \frac{1}{2}, -\frac{1\ddot{0}}{2\ddot{\theta}}}$	$-z K_d^{a, a_i} \mathfrak{C}_{\mathfrak{e}}^{n\ell 0, \frac{1}{2}, n1 \frac{1\ddot{0}}{2\ddot{\theta}_{1/2}}}$
$\mathfrak{C}_{\mathfrak{e}}^{n\ell, 0, \frac{1}{2}, -\frac{1\ddot{0}}{2\ddot{\theta}}}$	$\mathfrak{C}_{\mathfrak{e}}^{n, 1, \frac{3}{2}, \frac{3\ddot{0}}{2\ddot{\theta}}}$	0
$\mathfrak{C}_{\mathfrak{e}}^{n\ell, 0, \frac{1}{2}, -\frac{1\ddot{0}}{2\ddot{\theta}}}$	$\mathfrak{C}_{\mathfrak{e}}^{n, 1, \frac{3}{2}, \frac{1\ddot{0}}{2\ddot{\theta}}}$	$-\frac{1}{2}(x+iy) K_d^{a, a_i} \mathfrak{C}_{\mathfrak{e}}^{n\ell 0, \frac{1}{2}, n1 \frac{3\ddot{0}}{2\ddot{\theta}_{1/2}}}$
$\mathfrak{C}_{\mathfrak{e}}^{n\ell, 0, \frac{1}{2}, -\frac{1\ddot{0}}{2\ddot{\theta}}}$	$\mathfrak{C}_{\mathfrak{e}}^{n, 1, \frac{3}{2}, -\frac{1\ddot{0}}{2\ddot{\theta}}}$	$z K_d^{a, a_i} \mathfrak{C}_{\mathfrak{e}}^{n\ell 0, \frac{1}{2}, n1 \frac{3\ddot{0}}{2\ddot{\theta}_{1/2}}}$
$\mathfrak{C}_{\mathfrak{e}}^{n\ell, 0, \frac{1}{2}, -\frac{1\ddot{0}}{2\ddot{\theta}}}$	$\mathfrak{C}_{\mathfrak{e}}^{n, 1, \frac{3}{2}, -\frac{3\ddot{0}}{2\ddot{\theta}}}$	$\frac{\sqrt{3}}{2}(x-iy) K_d^{a, a_i} \mathfrak{C}_{\mathfrak{e}}^{n\ell 0, \frac{1}{2}, n1 \frac{3\ddot{0}}{2\ddot{\theta}_{1/2}}}$
$\mathfrak{C}_{\mathfrak{e}}^{n\ell, 1, \frac{1}{2}, \frac{1\ddot{0}}{2\ddot{\theta}}}$	$\mathfrak{C}_{\mathfrak{e}}^{n, 0, \frac{1}{2}, \frac{1\ddot{0}}{2\ddot{\theta}}}$	$z K_d^{a, a_i} \mathfrak{C}_{\mathfrak{e}}^{n\ell 1, \frac{1}{2}, n0 \frac{1\ddot{0}}{2\ddot{\theta}_{1/2}}}$
$\mathfrak{C}_{\mathfrak{e}}^{n\ell, 1, \frac{1}{2}, \frac{1\ddot{0}}{2\ddot{\theta}}}$	$\mathfrak{C}_{\mathfrak{e}}^{n, 0, \frac{1}{2}, -\frac{1\ddot{0}}{2\ddot{\theta}}}$	$(x-iy) K_d^{a, a_i} \mathfrak{C}_{\mathfrak{e}}^{n\ell 1, \frac{1}{2}, n0 \frac{1\ddot{0}}{2\ddot{\theta}_{1/2}}}$
$\mathfrak{C}_{\mathfrak{e}}^{n\ell, 1, \frac{1}{2}, \frac{1\ddot{0}}{2\ddot{\theta}}}$	$\mathfrak{C}_{\mathfrak{e}}^{n, 1, \frac{1}{2}, \frac{1\ddot{0}}{2\ddot{\theta}}}$	$K_d^{a, a_i} \mathfrak{C}_{\mathfrak{e}}^{n\ell 1, \frac{1}{2}, n1 \frac{1\ddot{0}}{2\ddot{\theta}_{1/2}}}$
$\mathfrak{C}_{\mathfrak{e}}^{n\ell, 1, \frac{1}{2}, \frac{1\ddot{0}}{2\ddot{\theta}}}$	$\mathfrak{C}_{\mathfrak{e}}^{n, 1, \frac{1}{2}, -\frac{1\ddot{0}}{2\ddot{\theta}}}$	0
$\mathfrak{C}_{\mathfrak{e}}^{n\ell, 1, \frac{1}{2}, \frac{1\ddot{0}}{2\ddot{\theta}}}$	$\mathfrak{C}_{\mathfrak{e}}^{n, 1, \frac{3}{2}, \frac{3\ddot{0}}{2\ddot{\theta}}}$	$-\frac{\sqrt{3}}{2} z(x+iy) K_d^{a, a_i} \mathfrak{C}_{\mathfrak{e}}^{n\ell 1, \frac{1}{2}, n1 \frac{3\ddot{0}}{2\ddot{\theta}_{1/2}}}$
$\mathfrak{C}_{\mathfrak{e}}^{n\ell, 1, \frac{1}{2}, \frac{1\ddot{0}}{2\ddot{\theta}}}$	$\mathfrak{C}_{\mathfrak{e}}^{n, 1, \frac{3}{2}, \frac{1\ddot{0}}{2\ddot{\theta}}}$	$\frac{1}{2}(3z^2-1) K_d^{a, a_i} \mathfrak{C}_{\mathfrak{e}}^{n\ell 1, \frac{1}{2}, n1 \frac{3\ddot{0}}{2\ddot{\theta}_{1/2}}}$
$\mathfrak{C}_{\mathfrak{e}}^{n\ell, 1, \frac{1}{2}, \frac{1\ddot{0}}{2\ddot{\theta}}}$	$\mathfrak{C}_{\mathfrak{e}}^{n, 1, \frac{3}{2}, -\frac{1\ddot{0}}{2\ddot{\theta}}}$	$\frac{3}{2} z(x-iy) K_d^{a, a_i} \mathfrak{C}_{\mathfrak{e}}^{n\ell 1, \frac{1}{2}, n1 \frac{3\ddot{0}}{2\ddot{\theta}_{1/2}}}$

$\mathfrak{C}n\ell, 1, \frac{3}{2}, \frac{3\ddot{0}}{2\ddot{\theta}}$	$\mathfrak{C}n, 1, \frac{1}{2}, -\frac{1\ddot{0}}{2\ddot{\theta}}$	$-\frac{\sqrt{3}}{2}(x-iy)^2 K_d^{a,a_i} \mathfrak{C}n\ell \frac{3}{2}, n1 \frac{1\ddot{0}}{2\ddot{\theta}_{1/2}}$
$\mathfrak{C}n\ell, 1, \frac{3}{2}, \frac{3\ddot{0}}{2\ddot{\theta}}$	$\mathfrak{C}n, 1, \frac{3}{2}, \frac{3\ddot{0}}{2\ddot{\theta}}$	$\frac{3}{4}(1-z^2)K_d^{a,a_i} \mathfrak{C}n\ell \frac{3}{2}, n1 \frac{3\ddot{0}}{2\ddot{\theta}_{1/2}} + \frac{1}{4}(1+3z^2)K_d^{a,a_i} \mathfrak{C}n\ell \frac{3}{2}, n1 \frac{3\ddot{0}}{2\ddot{\theta}_{3/2}}$
$\mathfrak{C}n\ell, 1, \frac{3}{2}, \frac{3\ddot{0}}{2\ddot{\theta}}$	$\mathfrak{C}n, 1, \frac{3}{2}, \frac{1\ddot{0}}{2\ddot{\theta}}$	$\frac{\sqrt{3}}{2}z(x-iy)\overset{\dot{\downarrow}}{\underset{\dot{\uparrow}}{K_d^{a,a_i}}} \mathfrak{C}n\ell \frac{3}{2}, n1 \frac{3\ddot{0}}{2\ddot{\theta}_{3/2}} - K_d^{a,a_i} \mathfrak{C}n\ell \frac{3}{2}, n1 \frac{3\ddot{0}}{2\ddot{\theta}_{1/2}} \overset{\ddot{u}}{\underset{\ddot{y}}{\overset{\ddot{p}}{\ddot{b}}}}$
$\mathfrak{C}n\ell, 1, \frac{3}{2}, \frac{3\ddot{0}}{2\ddot{\theta}}$	$\mathfrak{C}n, 1, \frac{3}{2}, -\frac{1\ddot{0}}{2\ddot{\theta}}$	$\frac{\sqrt{3}}{4}(x-iy)^2 \overset{\dot{\downarrow}}{\underset{\dot{\uparrow}}{K_d^{a,a_i}}} \mathfrak{C}n\ell \frac{3}{2}, n1 \frac{3\ddot{0}}{2\ddot{\theta}_{1/2}} - K_d^{a,a_i} \mathfrak{C}n\ell \frac{3}{2}, n1 \frac{3\ddot{0}}{2\ddot{\theta}_{3/2}} \overset{\ddot{u}}{\underset{\ddot{y}}{\overset{\ddot{p}}{\ddot{b}}}}$
$\mathfrak{C}n\ell, 1, \frac{3}{2}, \frac{3\ddot{0}}{2\ddot{\theta}}$	$\mathfrak{C}n, 1, \frac{3}{2}, -\frac{3\ddot{0}}{2\ddot{\theta}}$	0
$\mathfrak{C}n\ell, 1, \frac{3}{2}, \frac{1\ddot{0}}{2\ddot{\theta}}$	$\mathfrak{C}n, 0, \frac{1}{2}, \frac{1\ddot{0}}{2\ddot{\theta}}$	$z K_d^{a,a_i} \mathfrak{C}n\ell \frac{3}{2}, n0 \frac{1\ddot{0}}{2\ddot{\theta}_{1/2}}$
$\mathfrak{C}n\ell, 1, \frac{3}{2}, \frac{1\ddot{0}}{2\ddot{\theta}}$	$\mathfrak{C}n, 0, \frac{1}{2}, -\frac{1\ddot{0}}{2\ddot{\theta}}$	$-\frac{1}{2}(x-iy)K_d^{a,a_i} \mathfrak{C}n\ell \frac{3}{2}, n0 \frac{1\ddot{0}}{2\ddot{\theta}_{1/2}}$
$\mathfrak{C}n\ell, 1, \frac{3}{2}, \frac{1\ddot{0}}{2\ddot{\theta}}$	$\mathfrak{C}n, 1, \frac{1}{2}, \frac{1\ddot{0}}{2\ddot{\theta}}$	$\frac{1}{2}(3z^2-1)K_d^{a,a_i} \mathfrak{C}n\ell \frac{3}{2}, n1 \frac{1\ddot{0}}{2\ddot{\theta}_{1/2}}$
$\mathfrak{C}n\ell, 1, \frac{3}{2}, \frac{1\ddot{0}}{2\ddot{\theta}}$	$\mathfrak{C}n, 1, \frac{1}{2}, -\frac{1\ddot{0}}{2\ddot{\theta}}$	$\frac{3}{2}z(x-iy)K_d^{a,a_i} \mathfrak{C}n\ell \frac{3}{2}, n1 \frac{1\ddot{0}}{2\ddot{\theta}_{1/2}}$
$\mathfrak{C}n\ell, 1, \frac{3}{2}, \frac{1\ddot{0}}{2\ddot{\theta}}$	$\mathfrak{C}n, 1, \frac{3}{2}, \frac{3\ddot{0}}{2\ddot{\theta}}$	$\frac{\sqrt{3}}{2}z(x+iy)\overset{\dot{\downarrow}}{\underset{\dot{\uparrow}}{K_d^{a,a_i}}} \mathfrak{C}n\ell \frac{3}{2}, n1 \frac{3\ddot{0}}{2\ddot{\theta}_{3/2}} - K_d^{a,a_i} \mathfrak{C}n\ell \frac{3}{2}, n1 \frac{3\ddot{0}}{2\ddot{\theta}_{1/2}} \overset{\ddot{u}}{\underset{\ddot{y}}{\overset{\ddot{p}}{\ddot{b}}}}$
$\mathfrak{C}n\ell, 1, \frac{3}{2}, \frac{1\ddot{0}}{2\ddot{\theta}}$	$\mathfrak{C}n, 1, \frac{3}{2}, \frac{1\ddot{0}}{2\ddot{\theta}}$	$\frac{1}{4}(3z^2+1)K_d^{a,a_i} \mathfrak{C}n\ell \frac{3}{2}, n1 \frac{3\ddot{0}}{2\ddot{\theta}_{1/2}} + \frac{3}{4}(1-z^2)K_d^{a,a_i} \mathfrak{C}n\ell \frac{3}{2}, n1 \frac{3\ddot{0}}{2\ddot{\theta}_{3/2}}$
$\mathfrak{C}n\ell, 1, \frac{3}{2}, \frac{1\ddot{0}}{2\ddot{\theta}}$	$\mathfrak{C}n, 1, \frac{3}{2}, -\frac{1\ddot{0}}{2\ddot{\theta}}$	0

$\mathfrak{C}n\ell, 1, \frac{3}{2}, -\frac{1\ddot{0}}{2\ddot{\theta}}$	$\mathfrak{C}n, 1, \frac{3}{2}, -\frac{3\ddot{0}}{2\ddot{\theta}}$	$\frac{\sqrt{3}}{4}(x-iy)^2 \overset{\dot{\downarrow}}{\underset{\dot{\uparrow}}{K_d^{a_j a_i}}} \mathfrak{C}n\ell \frac{3}{2}, n1 \frac{3\ddot{0}}{2\ddot{\theta}_{3/2}} - K_d^{a_j a_i} \mathfrak{C}n\ell \frac{3}{2}, n1 \frac{3\ddot{0}}{2\ddot{\theta}_{1/2}} \overset{\ddot{u}}{\underset{\ddot{y}}{\overset{\ddot{p}}{\ddot{b}}}}$
$\mathfrak{C}n\ell, 1, \frac{3}{2}, -\frac{1\ddot{0}}{2\ddot{\theta}}$	$\mathfrak{C}n, 0, \frac{1}{2}, \frac{1\ddot{0}}{2\ddot{\theta}}$	$\frac{1}{2}(x+iy)K_d^{a_j a_i} \mathfrak{C}n\ell \frac{3}{2}, n0 \frac{1\ddot{0}}{2\ddot{\theta}_{1/2}}$
$\mathfrak{C}n\ell, 1, \frac{3}{2}, -\frac{1\ddot{0}}{2\ddot{\theta}}$	$\mathfrak{C}n, 0, \frac{1}{2}, -\frac{1\ddot{0}}{2\ddot{\theta}}$	$z K_d^{a_j a_i} \mathfrak{C}n\ell \frac{3}{2}, n0 \frac{1\ddot{0}}{2\ddot{\theta}_{1/2}}$
$\mathfrak{C}n\ell, 1, \frac{3}{2}, -\frac{1\ddot{0}}{2\ddot{\theta}}$	$\mathfrak{C}n, 1, \frac{1}{2}, \frac{1\ddot{0}}{2\ddot{\theta}}$	$\frac{3}{2}z(x+iy)K_d^{a_j a_i} \mathfrak{C}n\ell \frac{3}{2}, n1 \frac{1\ddot{0}}{2\ddot{\theta}_{1/2}}$
$\mathfrak{C}n\ell, 1, \frac{3}{2}, -\frac{1\ddot{0}}{2\ddot{\theta}}$	$\mathfrak{C}n, 1, \frac{1}{2}, -\frac{1\ddot{0}}{2\ddot{\theta}}$	$\frac{1}{2}(1-3z^2)K_d^{a_j a_i} \mathfrak{C}n\ell \frac{3}{2}, n1 \frac{1\ddot{0}}{2\ddot{\theta}_{1/2}}$
$\mathfrak{C}n\ell, 1, \frac{3}{2}, -\frac{1\ddot{0}}{2\ddot{\theta}}$	$\mathfrak{C}n, 1, \frac{3}{2}, \frac{3\ddot{0}}{2\ddot{\theta}}$	$\frac{\sqrt{3}}{4}(x+iy)^2 \overset{\dot{\downarrow}}{\underset{\dot{\uparrow}}{K_d^{a_j a_i}}} \mathfrak{C}n\ell \frac{3}{2}, n1 \frac{3\ddot{0}}{2\ddot{\theta}_{1/2}} - K_d^{a_j a_i} \mathfrak{C}n\ell \frac{3}{2}, n1 \frac{3\ddot{0}}{2\ddot{\theta}_{3/2}} \overset{\ddot{u}}{\underset{\ddot{y}}{\overset{\ddot{p}}{\ddot{b}}}}$
$\mathfrak{C}n\ell, 1, \frac{3}{2}, -\frac{1\ddot{0}}{2\ddot{\theta}}$	$\mathfrak{C}n, 1, \frac{3}{2}, \frac{1\ddot{0}}{2\ddot{\theta}}$	0
$\mathfrak{C}n\ell, 1, \frac{3}{2}, -\frac{1\ddot{0}}{2\ddot{\theta}}$	$\mathfrak{C}n, 1, \frac{3}{2}, -\frac{1\ddot{0}}{2\ddot{\theta}}$	$\frac{1}{4}(1+3z^2)K_d^{a_j a_i} \mathfrak{C}n\ell \frac{3}{2}, n1 \frac{3\ddot{0}}{2\ddot{\theta}_{1/2}} + \frac{3}{4}(1-z^2)K_d^{a_j a_i} \mathfrak{C}n\ell \frac{3}{2}, n1 \frac{3\ddot{0}}{2\ddot{\theta}_{3/2}}$
$\mathfrak{C}n\ell, 1, \frac{3}{2}, -\frac{1\ddot{0}}{2\ddot{\theta}}$	$\mathfrak{C}n, 1, \frac{3}{2}, -\frac{3\ddot{0}}{2\ddot{\theta}}$	$\frac{\sqrt{3}}{2}z(x-iy) \overset{\dot{\downarrow}}{\underset{\dot{\uparrow}}{K_d^{a_j a_i}}} \mathfrak{C}n\ell \frac{3}{2}, n1 \frac{3\ddot{0}}{2\ddot{\theta}_{1/2}} - K_d^{a_j a_i} \mathfrak{C}n\ell \frac{3}{2}, n1 \frac{3\ddot{0}}{2\ddot{\theta}_{3/2}} \overset{\ddot{u}}{\underset{\ddot{y}}{\overset{\ddot{p}}{\ddot{b}}}}$
$\mathfrak{C}n\ell, 1, \frac{3}{2}, -\frac{3\ddot{0}}{2\ddot{\theta}}$	$\mathfrak{C}n, 0, \frac{1}{2}, \frac{1\ddot{0}}{2\ddot{\theta}}$	0
$\mathfrak{C}n\ell, 1, \frac{3}{2}, -\frac{3\ddot{0}}{2\ddot{\theta}}$	$\mathfrak{C}n, 0, \frac{1}{2}, -\frac{1\ddot{0}}{2\ddot{\theta}}$	$\frac{\sqrt{3}}{2}(x+iy)K_d^{a_j a_i} \mathfrak{C}n\ell \frac{3}{2}, n0 \frac{1\ddot{0}}{2\ddot{\theta}_{1/2}}$
$\mathfrak{C}n\ell, 1, \frac{3}{2}, -\frac{3\ddot{0}}{2\ddot{\theta}}$	$\mathfrak{C}n, 1, \frac{1}{2}, \frac{1\ddot{0}}{2\ddot{\theta}}$	$\frac{\sqrt{3}}{2}(x+iy)^2 K_d^{a_j a_i} \mathfrak{C}n\ell \frac{3}{2}, n1 \frac{1\ddot{0}}{2\ddot{\theta}_{1/2}}$

$\begin{matrix} \square \\ \square \end{matrix} n, 1, \frac{3}{2}, \frac{3}{2}$	$\begin{matrix} \square \\ \square \end{matrix} n, 1, \frac{1}{2}, \frac{1}{2}$	$\frac{\sqrt{3}}{2} z(x+iy) K_d^{a_j a_i} \begin{matrix} \square \\ \square \end{matrix} n, 1, \frac{3}{2}, n, 1, \frac{1}{2}$
$\begin{matrix} \square \\ \square \end{matrix} n, 1, \frac{3}{2}, \frac{3}{2}$	$\begin{matrix} \square \\ \square \end{matrix} n, 1, \frac{3}{2}, \frac{3}{2}$	0
$\begin{matrix} \square \\ \square \end{matrix} n, 1, \frac{3}{2}, \frac{3}{2}$	$\begin{matrix} \square \\ \square \end{matrix} n, 1, \frac{3}{2}, \frac{1}{2}$	$\frac{\sqrt{3}}{4} (x+iy)^2 K_d^{a_j a_i} \begin{matrix} \square \\ \square \end{matrix} n, 1, \frac{3}{2}, n, 1, \frac{3}{2} \begin{matrix} \square \\ \square \end{matrix} K_d^{a_j a_i} \begin{matrix} \square \\ \square \end{matrix} n, 1, \frac{3}{2}, n, 1, \frac{3}{2}$
$\begin{matrix} \square \\ \square \end{matrix} n, 1, \frac{3}{2}, \frac{3}{2}$	$\begin{matrix} \square \\ \square \end{matrix} n, 1, \frac{3}{2}, \frac{1}{2}$	$\frac{\sqrt{3}}{2} z(x+iy) K_d^{a_j a_i} \begin{matrix} \square \\ \square \end{matrix} n, 1, \frac{3}{2}, n, 1, \frac{3}{2} \begin{matrix} \square \\ \square \end{matrix} K_d^{a_j a_i} \begin{matrix} \square \\ \square \end{matrix} n, 1, \frac{3}{2}, n, 1, \frac{3}{2}$
$\begin{matrix} \square \\ \square \end{matrix} n, 1, \frac{3}{2}, \frac{3}{2}$	$\begin{matrix} \square \\ \square \end{matrix} n, 1, \frac{3}{2}, \frac{3}{2}$	$\frac{3}{4} (1+z^2) K_d^{a_j a_i} \begin{matrix} \square \\ \square \end{matrix} n, 1, \frac{3}{2}, n, 1, \frac{3}{2} + \frac{1}{4} (1+3z^2) K_d^{a_j a_i} \begin{matrix} \square \\ \square \end{matrix} n, 1, \frac{3}{2}, n, 1, \frac{3}{2}$

2.5 Determination of relativistic TB parameters

In this section, we explain how to determine the values of relativistic TB parameters. The relativistic TB parameters between the nearest neighbor atoms are determined for the crystalline silicon, bearing in mind that the MFRTB method will be actually applied to crystalline silicon immersed in the uniform magnetic field (Chapter 5). At first, Eq. (2.22) is applied to a crystalline silicon with taking into consideration the hopping integrals between the outermost shells of the nearest neighboring atoms. Namely, the following eight kinds of relativistic atomic orbitals for each silicon atom are taken into consideration.

$$(n, \ell, J, M) = \left(3, 0, \frac{1}{2}, \pm \frac{1}{2}\right), \left(3, 1, \frac{1}{2}, \pm \frac{1}{2}\right), \left(3, 1, \frac{3}{2}, \pm \frac{1}{2}\right), \left(3, 1, \frac{3}{2}, \pm \frac{3}{2}\right). \quad (2.96)$$

The Hamiltonian matrix thus obtained has the dimension of 16×16 because there are two silicon atoms in the unit cell. Next, the relativistic TB parameters are determined by requiring that the eigenvalues of the Hamiltonian matrix coincide with the reference data as well as possible. As the reference data, we utilize results calculated by fully RLAPW method [24,27,28]. As for $\bar{\varepsilon}_{n\ell J}^{Si} + \Delta \bar{\varepsilon}_{n\ell JM}^{Si, d_i}$ that is included in Eq. (2.22), since the energy of the crystal field is much smaller than the atomic spectrum, we neglect $\Delta \bar{\varepsilon}_{n\ell JM}^{Si, d_i}$ and employ the atomic spectrum calculated on the basis of density functional theory [42,43] with the local density

approximation [43]. The numerical values of relativistic TB parameters and $\bar{\varepsilon}_{n\ell J}^{Si} + \Delta\bar{\varepsilon}_{n\ell JM}^{Si,d_i}$ thus determined are listed in Table-II and III, respectively.

With the help of above data listed in Tables-II and III, the actual electronic structure of silicon E_k in the absence of magnetic field (zero magnetic field) is performed which is shown in Fig. (2.1).

Table-II. Relativistic TB parameters between the nearest neighbor atoms for the crystalline Silicon.

(n, ℓ, J, M)	Numerical values (eV)
$K\left(n'0 \frac{1}{2}, n0 \frac{1}{2}\right)_{1/2}$	-1.7391
$K\left(n'0 \frac{1}{2}, n1 \frac{1}{2}\right)_{1/2}$	-1.2038
$K\left(n'0 \frac{1}{2}, n1 \frac{3}{2}\right)_{1/2}$	-1.7048
$K\left(n'1 \frac{1}{2}, n1 \frac{1}{2}\right)_{1/2}$	0.26962
$K\left(n'1 \frac{1}{2}, n1 \frac{3}{2}\right)_{1/2}$	-1.8830
$K\left(n'1 \frac{3}{2}, n1 \frac{1}{2}\right)_{1/2}$	-1.5978
$K\left(n'1 \frac{3}{2}, n1 \frac{3}{2}\right)_{3/2}$	-1.06233

Table-III. Numerical values of $\bar{\varepsilon}_{n\ell J}^{Si} + \Delta\bar{\varepsilon}_{n\ell JM}^{Si,d_i}$ for the Silicon atom.

(n, ℓ, J, M)	Numerical values (eV)
$\left(3, 0, \frac{1}{2}, \pm \frac{1}{2}\right)$	-12.1538
$\left(3, 1, \frac{1}{2}, \pm \frac{1}{2}\right)$	-5.6148
$\left(3, 1, \frac{3}{2}, \pm \frac{1}{2}\right), \left(3, 1, \frac{3}{2}, \pm \frac{3}{2}\right)$	-5.5853

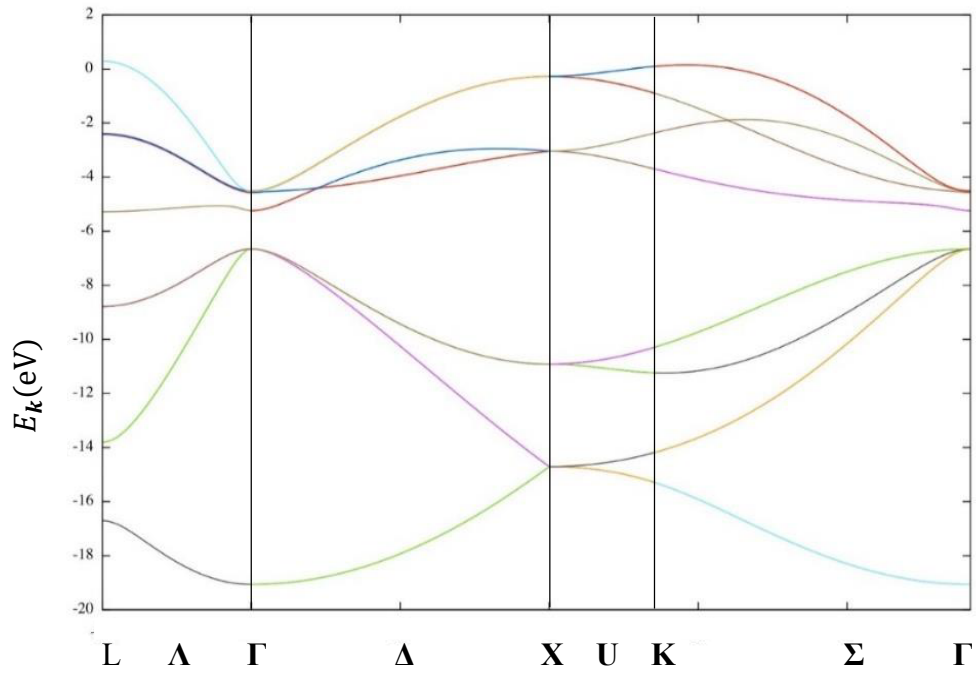


Fig. 2.1 Energy dispersion for a crystalline silicon in the absence of magnetic field. The labels in the horizontal axis denote the special k points in the first Brillouin zone

Chapter 3

Magnetic Field Containing Relativistic Tight Binding (MFRTB) Approximation Method

3.1 Matrix elements of Hamiltonian

Consider the crystalline material immersed in the uniform magnetic field. The electrons in the system feel not only the electric field, which is created by periodically aligned atoms, but also the magnetic field. Consider the Dirac equation for an electron is [39]

$$H\Phi_{\mathbf{k}}(\mathbf{r}) = E_{\mathbf{k}}\Phi_{\mathbf{k}}(\mathbf{r}) \quad (3.1)$$

with

$$H = c\boldsymbol{\alpha} \cdot \{\mathbf{p} + e\mathbf{A}(\mathbf{r})\} + \beta mc^2 + \sum_{\mathbf{R}_n} \sum_i V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i), \quad (3.2)$$

where e , $\mathbf{A}(\mathbf{r})$, $V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i)$ denote the elementary charge, vector potential of the uniform magnetic field \mathbf{B} and the scalar potential caused by the nucleus of an atom a_i , the center of which is located at $\mathbf{R}_n + \mathbf{d}_i$, respectively. The definitions of vectors \mathbf{R}_n and \mathbf{d}_i are same as in Eq. (2.2) in Chapter 2. Let us suppose a uniform magnetic field \mathbf{B} is applied along the z -axis, and the Landau gauge is employed for $\mathbf{A}(\mathbf{r})$, i.e.,

$$\mathbf{A}(\mathbf{r}) = (0, Bx, 0), \quad (3.3)$$

where B is the magnitude of magnetic field. The four-component wave function for an electron in the uniform magnetic field is denoted by $\Phi_{\mathbf{k}}(\mathbf{r})$ in Eq. (3.1), where the subscript \mathbf{k} is the quantum number related to the magnetic Bloch theorem which will be discussed in Chapters 4, 5 and 6. In order to develop the MFRTB method, $\Phi_{\mathbf{k}}(\mathbf{r})$ is expanded by using as a basis function of the relativistic wave function of atoms immersed in the uniform magn-

netic field. The Dirac equation for an atom immersed in the uniform magnetic field and located at $\mathbf{R}_n + \mathbf{d}_i$, is given by

$$\left[c\boldsymbol{\alpha} \cdot \{ \mathbf{p} + e\mathbf{A}(\mathbf{r}) + \} + \beta mc^2 + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i) \right] \psi_{\xi}^{a_i, \mathbf{R}_n + \mathbf{d}_i}(\mathbf{r}) = \varepsilon_{\xi}^{a_i, \mathbf{R}_n + \mathbf{d}_i} \psi_{\xi}^{a_i, \mathbf{R}_n + \mathbf{d}_i}(\mathbf{r}), \quad (3.4)$$

where $\psi_{\xi}^{a_i, \mathbf{R}_n + \mathbf{d}_i}(\mathbf{r})$ and $\varepsilon_{\xi}^{a_i, \mathbf{R}_n + \mathbf{d}_i}$ denote the relativistic atomic orbital and atomic spectrum in the uniform magnetic field. The subscript ξ in $\psi_{\xi}^{a_i, \mathbf{R}_n + \mathbf{d}_i}(\mathbf{r})$ and $\varepsilon_{\xi}^{a_i, \mathbf{R}_n + \mathbf{d}_i}$ is the quantum number in the atomic system. Expanding $\Phi_k(\mathbf{r})$ in terms of $\psi_{\xi}^{a_i, \mathbf{R}_n + \mathbf{d}_i}(\mathbf{r})$, we have

$$\Phi_k(\mathbf{r}) = \sum_{\mathbf{R}_n} \sum_i \sum_{\xi} C_k^{\xi}(\mathbf{R}_n + \mathbf{d}_i) \psi_{\xi}^{a_i, \mathbf{R}_n + \mathbf{d}_i}(\mathbf{r}), \quad (3.5)$$

where $C_k^{\xi}(\mathbf{R}_n + \mathbf{d}_i)$ is the expansion coefficients that should be determined. Substituting Eq. (3.5) into Eq. (3.1), we have

$$\sum_{\mathbf{R}_n} \sum_i \sum_{\xi} C_k^{\xi}(\mathbf{R}_n + \mathbf{d}_i) H \psi_{\xi}^{a_i, \mathbf{R}_n + \mathbf{d}_i}(\mathbf{r}) = E_k \sum_{\mathbf{R}_n} \sum_i \sum_{\xi} C_k^{\xi}(\mathbf{R}_n + \mathbf{d}_i) \psi_{\xi}^{a_i, \mathbf{R}_n + \mathbf{d}_i}(\mathbf{r}). \quad (3.6)$$

Multiplying $\psi_{\eta}^{a_j, \mathbf{R}_m + \mathbf{d}_j}(\mathbf{r})^{\dagger}$ on both sides of Eq. (3.6) and integrating with respect to \mathbf{r} , we get

$$\sum_{\mathbf{R}_n} \sum_i \sum_{\xi} C_k^{\xi}(\mathbf{R}_n + \mathbf{d}_i) H_{\mathbf{R}_m j \eta, \mathbf{R}_n i \xi} = E_k C_k^{\eta}(\mathbf{R}_m + \mathbf{d}_j), \quad (3.7)$$

with

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

where, similar to the conventional [41] and relativistic TB methods (Chapter 2), we use the following approximation concerning the relativistic atomic orbitals:

$$\int \psi_{\eta}^{a_j, \mathbf{R}_m + \mathbf{d}_j}(\mathbf{r}) \psi_{\xi}^{a_i, \mathbf{R}_n + \mathbf{d}_i}(\mathbf{r}) d^3 r \approx \delta_{\mathbf{R}_m, \mathbf{R}_n} \delta_{j,i} \delta_{\eta, \xi}. \quad (3.9)$$

Equation (3.9) means that the overlap between the relativistic atomic orbitals centered on different atoms becomes negligible. Let us rewrite Eq. (3.8) by rewriting the Dirac Hamiltonian [Eq. (2.3)] in the uniform magnetic field as

$$H = \frac{1}{2} \left\{ c\boldsymbol{\alpha} \cdot \{ \mathbf{p} + e\mathbf{A}(\mathbf{r}) + \} + \beta mc^2 + V_{a_j}(\mathbf{r} - \mathbf{R}_m - \mathbf{d}_j) + \sum_{\ell \neq j} V_{a_{\ell}}(\mathbf{r} - \mathbf{R}_m - \mathbf{d}_{\ell}) \right. \\ \left. + \sum_{k \neq m} \sum_{\ell} V_{a_{\ell}}(\mathbf{r} - \mathbf{R}_k - \mathbf{d}_{\ell}) + \frac{1}{2} \{ c\boldsymbol{\alpha} \cdot \{ \mathbf{p} + e\mathbf{A}(\mathbf{r}) + \} + \beta mc^2 + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i) \right\}$$

$$+ \left. \sum_{\ell \neq i} V_{a_\ell}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_\ell) + \sum_{k \neq n} \sum_{\ell} V_{a_\ell}(\mathbf{r} - \mathbf{R}_k - \mathbf{d}_\ell) \right\} \quad (3.10)$$

Substituting Eq. (3.10) into Eq. (3.9), and using Eq. (3.4), we have

$$\begin{aligned} H_{\mathbf{R}_m j \eta, \mathbf{R}_n i \xi} &= \frac{1}{2} \mathcal{E}_\xi^{a_j, \mathbf{R}_m + \mathbf{d}_j} \delta_{\mathbf{R}_m, \mathbf{R}_n} \delta_{j,i} \delta_{\eta, \xi} + \frac{1}{2} \mathcal{E}_\xi^{a_i, \mathbf{R}_n + \mathbf{d}_i} \delta_{\mathbf{R}_m, \mathbf{R}_n} \delta_{j,i} \delta_{\eta, \xi} \\ &+ \frac{1}{2} \sum_{\ell \neq \mu} \int \psi_\eta^{a_j, \mathbf{R}_m + \mathbf{d}_j}(\mathbf{r})^\dagger V_{a_\ell}(\mathbf{r} - \mathbf{R}_m - \mathbf{d}_\ell) \psi_\xi^{a_i, \mathbf{R}_n + \mathbf{d}_i}(\mathbf{r}) d^3 r \\ &+ \frac{1}{2} \sum_{\ell \neq \nu} \int \psi_\eta^{a_j, \mathbf{R}_m + \mathbf{d}_j}(\mathbf{r})^\dagger V_{a_\ell}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_\ell) \psi_\xi^{a_i, \mathbf{R}_n + \mathbf{d}_i}(\mathbf{r}) d^3 r \\ &+ \frac{1}{2} \sum_{k \neq m} \sum_{\ell} \int \psi_\eta^{a_j, \mathbf{R}_m + \mathbf{d}_j}(\mathbf{r})^\dagger V_{a_\ell}(\mathbf{r} - \mathbf{R}_k - \mathbf{d}_\ell) \psi_\xi^{a_i, \mathbf{R}_n + \mathbf{d}_i}(\mathbf{r}) d^3 r \\ &+ \frac{1}{2} \sum_{k \neq n} \sum_{\ell} \int \psi_\eta^{a_j, \mathbf{R}_m + \mathbf{d}_j}(\mathbf{r})^\dagger V_{a_\ell}(\mathbf{r} - \mathbf{R}_k - \mathbf{d}_\ell) \psi_\xi^{a_i, \mathbf{R}_n + \mathbf{d}_i}(\mathbf{r}) d^3 r \end{aligned} \quad (3.11)$$

Let us rewrite Eq. (3.11) one by one

(i) $\mathbf{R}_m + \mathbf{d}_j = \mathbf{R}_n + \mathbf{d}_i$, then Eq. (3.11) becomes,

$$\begin{aligned} H_{\mathbf{R}_m j \eta, \mathbf{R}_n i \xi} &= \mathcal{E}_\xi^{a_i, \mathbf{R}_n + \mathbf{d}_i} \delta_{\eta, \xi} + \sum_{\ell \neq i} \int \psi_\eta^{a_i, \mathbf{R}_n + \mathbf{d}_i}(\mathbf{r})^\dagger V_{a_\ell}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_\ell) \psi_\xi^{a_i, \mathbf{R}_n + \mathbf{d}_i}(\mathbf{r}) d^3 r \\ &+ \sum_{k \neq n} \sum_{\ell} \int \psi_\eta^{a_i, \mathbf{R}_n + \mathbf{d}_i}(\mathbf{r})^\dagger V_{a_\ell}(\mathbf{r} - \mathbf{R}_k - \mathbf{d}_\ell) \psi_\xi^{a_i, \mathbf{R}_n + \mathbf{d}_i}(\mathbf{r}) d^3 r. \end{aligned} \quad (3.12)$$

The second and third term of RHS of Eq. (3.12) denote the energy of the crystal field. This fact can be confirmed by rewriting these terms as

$$\int \psi_\eta^{a_i, \mathbf{R}_n + \mathbf{d}_i}(\mathbf{r})^\dagger \left\{ \sum_{\substack{\mathbf{R}_k \\ (\mathbf{R}_k + \mathbf{d}_\ell \neq \mathbf{R}_n + \mathbf{d}_i)}} \sum_{\ell} V_{a_\ell}(\mathbf{r} - \mathbf{R}_k - \mathbf{d}_\ell) \right\} \psi_\xi^{a_i, \mathbf{R}_n + \mathbf{d}_i}(\mathbf{r}) d^3 r.$$

Since $\psi_\eta^{a_i, \mathbf{R}_n + \mathbf{d}_i}(\mathbf{r})$ and $\psi_\xi^{a_i, \mathbf{R}_n + \mathbf{d}_i}(\mathbf{r})$ are localized around $\mathbf{R}_n + \mathbf{d}_i$, that is different from $\mathbf{R}_k + \mathbf{d}_\ell$, we may approximate the above integral by replacing $V_{a_\ell}(\mathbf{r} - \mathbf{R}_k - \mathbf{d}_\ell)$ with $V_{a_\ell}(\mathbf{R}_n + \mathbf{d}_i - \mathbf{R}_k - \mathbf{d}_\ell)$. This approximation immediately leads to

$$\int \psi_\eta^{a_i, \mathbf{R}_n + \mathbf{d}_i}(\mathbf{r})^\dagger \left\{ \sum_{\substack{\mathbf{R}_k \\ (\mathbf{R}_k + \mathbf{d}_\ell \neq \mathbf{R}_n + \mathbf{d}_i)}} \sum_{\ell} V_{a_\ell}(\mathbf{R}_n + \mathbf{d}_i - \mathbf{R}_k - \mathbf{d}_\ell) \right\} \psi_\xi^{a_i, \mathbf{R}_n + \mathbf{d}_i}(\mathbf{r}) d^3 r = \Delta \mathcal{E}_\xi^{a_i, \mathbf{R}_n + \mathbf{d}_i} \delta_{\eta, \xi}, \quad (2.13)$$

with

$$\Delta \mathcal{E}_\xi^{a_i, \mathbf{R}_n + \mathbf{d}_i} = \int \psi_\xi^{a_i, \mathbf{R}_n + \mathbf{d}_i}(\mathbf{r})^\dagger \left\{ \sum_{\substack{\mathbf{R}_k \\ (\mathbf{R}_k + \mathbf{d}_\ell \neq \mathbf{R}_n + \mathbf{d}_i)}} \sum_{\ell} V_{a_\ell}(\mathbf{R}_n + \mathbf{d}_i - \mathbf{R}_k - \mathbf{d}_\ell) \right\} \psi_\xi^{a_i, \mathbf{R}_n + \mathbf{d}_i}(\mathbf{r}) d^3 r \quad (2.14)$$

Substituting Eq. (3.13) into Eq. (3.12), we have

$$H_{\mathbf{R}_m j \eta, \mathbf{R}_n i \xi} = (\mathcal{E}_{\xi}^{a_i, \mathbf{R}_n + \mathbf{d}_i} + \Delta \mathcal{E}_{\xi}^{a_i, \mathbf{R}_n + \mathbf{d}_i}) \delta_{\eta \xi} \quad (3.15)$$

(ii) $\mathbf{R}_m + \mathbf{d}_j \square \mathbf{R}_n + \mathbf{d}_i$, then Eq. (3.11) becomes

$$\begin{aligned} H_{\mathbf{R}_m j \eta, \mathbf{R}_n i \xi} &= \frac{1}{2} \sum_{\ell \neq j} \int \psi_{\eta}^{a_j, \mathbf{R}_m + \mathbf{d}_j}(\mathbf{r})^{\dagger} V_{a_{\ell}}(\mathbf{r} - \mathbf{R}_m - \mathbf{d}_{\ell}) \psi_{\xi}^{a_i, \mathbf{R}_n + \mathbf{d}_i}(\mathbf{r}) d^3 r \\ &+ \frac{1}{2} \sum_{\ell \neq i} \int \psi_{\eta}^{a_j, \mathbf{R}_m + \mathbf{d}_j}(\mathbf{r})^{\dagger} V_{a_{\ell}}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_{\ell}) \psi_{\xi}^{a_i, \mathbf{R}_n + \mathbf{d}_i}(\mathbf{r}) d^3 r \\ &+ \frac{1}{2} \sum_{k \neq m} \sum_{\ell} \int \psi_{\eta}^{a_j, \mathbf{R}_m + \mathbf{d}_j}(\mathbf{r})^{\dagger} V_{a_{\ell}}(\mathbf{r} - \mathbf{R}_k - \mathbf{d}_{\ell}) \psi_{\xi}^{a_i, \mathbf{R}_n + \mathbf{d}_i}(\mathbf{r}) d^3 r \\ &+ \frac{1}{2} \sum_{k \neq n} \sum_{\ell} \int \psi_{\eta}^{a_j, \mathbf{R}_m + \mathbf{d}_j}(\mathbf{r})^{\dagger} V_{a_{\ell}}(\mathbf{r} - \mathbf{R}_k - \mathbf{d}_{\ell}) \psi_{\xi}^{a_i, \mathbf{R}_n + \mathbf{d}_i}(\mathbf{r}) d^3 r. \end{aligned} \quad (3.16)$$

The first and second terms correspond to the integrals involving three centers. Since these integrals are generally smaller than those involving two different centers or one center, we neglect the first and second term of Eq. (3.16). Let us take the third term of Eq. (3.16), we have

$$\begin{aligned} &\frac{1}{2} \sum_{k \neq m} \sum_{\ell} \int \psi_{\eta}^{a_j, \mathbf{R}_m + \mathbf{d}_j}(\mathbf{r})^{\dagger} V_{a_{\ell}}(\mathbf{r} - \mathbf{R}_k - \mathbf{d}_{\ell}) \psi_{\xi}^{a_i, \mathbf{R}_n + \mathbf{d}_i}(\mathbf{r}) d^3 r \\ &= \frac{1}{2} \int \psi_{\eta}^{a_j, \mathbf{R}_m + \mathbf{d}_j}(\mathbf{r})^{\dagger} V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i) \psi_{\xi}^{a_i, \mathbf{R}_n + \mathbf{d}_i}(\mathbf{r}) d^3 r \\ &+ \frac{1}{2} \sum_{k \neq m} \sum_n \int \psi_{\eta}^{a_j, \mathbf{R}_m + \mathbf{d}_j}(\mathbf{r})^{\dagger} V_{a_v}(\mathbf{r} - \mathbf{R}_k - \mathbf{d}_i) \psi_{\xi}^{a_i, \mathbf{R}_n + \mathbf{d}_i}(\mathbf{r}) d^3 r \\ &+ \frac{1}{2} \sum_{k \neq m} \sum_{\ell \neq i} \int \psi_{\eta}^{a_j, \mathbf{R}_m + \mathbf{d}_j}(\mathbf{r})^{\dagger} V_{a_{\ell}}(\mathbf{r} - \mathbf{R}_k - \mathbf{d}_{\ell}) \psi_{\xi}^{a_i, \mathbf{R}_n + \mathbf{d}_i}(\mathbf{r}) d^3 r. \end{aligned} \quad (3.17)$$

We neglect the integrals involving three different centers (last two integrals) of Eq. (3.17), since they are generally small compared to integrals involving two centers or the same centers. This approximation has been usually adopted in the conventional [41] and relativistic TB methods (Chapter 2). Thus, we have

$$\begin{aligned} &\frac{1}{2} \sum_{k \neq m} \sum_{\ell} \int \psi_{\eta}^{a_j, \mathbf{R}_m + \mathbf{d}_j}(\mathbf{r})^{\dagger} V_{a_{\ell}}(\mathbf{r} - \mathbf{R}_k - \mathbf{d}_{\ell}) \psi_{\xi}^{a_i, \mathbf{R}_n + \mathbf{d}_i}(\mathbf{r}) d^3 r \\ &\approx \frac{1}{2} \int \psi_{\eta}^{a_j, \mathbf{R}_m + \mathbf{d}_j}(\mathbf{r})^{\dagger} V_{a_i}(\mathbf{r} - \mathbf{R}_k - \mathbf{d}_i) \psi_{\xi}^{a_i, \mathbf{R}_n + \mathbf{d}_i}(\mathbf{r}) d^3 r \end{aligned} \quad (3.18)$$

Similarly, let us take fourth term of Eq. (3.16), we have

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

$$\begin{aligned}
&= \frac{1}{2} \int \psi_{\eta}^{a_j, \mathbf{R}_m + \mathbf{d}_j}(\mathbf{r})^\dagger V_{a_j}(\mathbf{r} - \mathbf{R}_m - \mathbf{d}_j) \psi_{\xi}^{a_i, \mathbf{R}_n + \mathbf{d}_i}(\mathbf{r}) d^3 r \\
&+ \frac{1}{2} \sum_{k \neq m, n} \int \psi_{\eta}^{a_j, \mathbf{R}_m + \mathbf{d}_j}(\mathbf{r})^\dagger V_{a_\mu}(\mathbf{r} - \mathbf{R}_k - \mathbf{d}_\mu) \psi_{\xi}^{a_i, \mathbf{R}_n + \mathbf{d}_i}(\mathbf{r}) d^3 r \\
&+ \frac{1}{2} \sum_{k \neq m} \sum_{\ell \neq j} \int \psi_{\eta}^{a_j, \mathbf{R}_m + \mathbf{d}_j}(\mathbf{r})^\dagger V_{a_\ell}(\mathbf{r} - \mathbf{R}_k - \mathbf{d}_\ell) \psi_{\xi}^{a_i, \mathbf{R}_n + \mathbf{d}_i}(\mathbf{r}) d^3 r \quad (3.19)
\end{aligned}$$

Again we neglect the integrals involving three different centers of Eq. (3.19), we get

$$\begin{aligned}
&\frac{1}{2} \sum_{k \neq n} \sum_{\ell} \int \psi_{\eta}^{a_j, \mathbf{R}_m + \mathbf{d}_j}(\mathbf{r})^\dagger V_{a_\ell}(\mathbf{r} - \mathbf{R}_k - \mathbf{d}_\ell) \psi_{\xi}^{a_i, \mathbf{R}_n + \mathbf{d}_i}(\mathbf{r}) d^3 r \\
&\approx \frac{1}{2} \int \psi_{\eta}^{a_j, \mathbf{R}_m + \mathbf{d}_j}(\mathbf{r})^\dagger V_{a_j}(\mathbf{r} - \mathbf{R}_m - \mathbf{d}_j) \psi_{\xi}^{a_i, \mathbf{R}_n + \mathbf{d}_i}(\mathbf{r}) d^3 r \quad (3.20)
\end{aligned}$$

Using Eqs. (3.18) and (3.20) into Eq. (3.16), we have

$$H_{\mathbf{R}_m j \eta, \mathbf{R}_n i \xi} = \int \psi_{\eta}^{a_j, \mathbf{R}_m + \mathbf{d}_j}(\mathbf{r})^\dagger \left(\frac{V_{a_j}(\mathbf{r} - \mathbf{R}_m - \mathbf{d}_j) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i)}{2} \right) \psi_{\xi}^{a_i, \mathbf{R}_n + \mathbf{d}_i}(\mathbf{r}) d^3 r. \quad (3.21)$$

Finally summarizing two cases [Eqs. (3.15) and (3.21)], we get the Hamiltonian matrix [Eq. (3.8)] as

$$\begin{aligned}
H_{\mathbf{R}_m j \eta, \mathbf{R}_n i \xi} &= (\mathcal{E}_{\xi}^{a_i, \mathbf{R}_n + \mathbf{d}_i} + \Delta \mathcal{E}_{\xi}^{a_i, \mathbf{R}_n + \mathbf{d}_i}) \delta_{j,i} \delta_{\mathbf{R}_m, \mathbf{R}_n} \delta_{\eta, \xi} + (1 - \delta_{\mathbf{R}_m, \mathbf{R}_n} \delta_{j,i}) \\
&\times \int \psi_{\eta}^{a_j, \mathbf{R}_m + \mathbf{d}_j}(\mathbf{r})^\dagger \left(\frac{V_{a_j}(\mathbf{r} - \mathbf{R}_m - \mathbf{d}_j) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i)}{2} \right) \psi_{\xi}^{a_i, \mathbf{R}_n + \mathbf{d}_i}(\mathbf{r}) d^3 r. \quad (3.22)
\end{aligned}$$

In order to simplify Eq. (3.20), let us consider the properties of $\psi_{\xi}^{a_i, \mathbf{R}_n + \mathbf{d}_i}(\mathbf{r})$ and $\mathcal{E}_{\xi}^{a_i, \mathbf{R}_n + \mathbf{d}_i}$. From Eq. (3.4), the Dirac equation for an atom immersed in the uniform magnetic field and located at the origin is given by

$$\left[c\boldsymbol{\alpha} \cdot \{ \mathbf{p} + e\mathbf{A}(\mathbf{r}) \} + \beta mc^2 + V_{a_i}(\mathbf{r}) \right] \psi_{\xi}^{a_i, 0}(\mathbf{r}) = \mathcal{E}_{\xi}^{a_i, 0} \psi_{\xi}^{a_i, 0}(\mathbf{r}). \quad (3.23)$$

By changing the variable \mathbf{r} to $\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i$, Eq. (3.23) is rewritten as

$$\begin{aligned}
&\left[c\boldsymbol{\alpha} \cdot \{ \mathbf{p} + e\mathbf{A}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i) \} + \beta mc^2 + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i) \right] \psi_{\xi}^{a_i, 0}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i) \\
&= \mathcal{E}_{\xi}^{a_i, 0} \psi_{\xi}^{a_i, 0}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i). \quad (3.24)
\end{aligned}$$

It should be noted that $\mathbf{A}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i)$ yields the same uniform magnetic field \mathbf{B} as $\mathbf{A}(\mathbf{r})$. Therefore, $\mathbf{A}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i)$ and $\mathbf{A}(\mathbf{r})$ are related by the gauge transformation such that

$$A(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i) = A(\mathbf{r}) + \nabla \chi(\mathbf{r}, \mathbf{R}_n + \mathbf{d}_i), \quad (3.25)$$

where $\chi(\mathbf{r}, \mathbf{R}_n + \mathbf{d}_i)$ is a function of both \mathbf{r} and $\mathbf{R}_n + \mathbf{d}_i$. Substituting Eq. (3.3) into Eq. (3.25) leads to

$$\chi(\mathbf{r}, \mathbf{R}_n + \mathbf{d}_i) = -B(R_{nx} + d_{ix})y, \quad (3.26)$$

where R_{nx} and d_{ix} denote the x -components of \mathbf{R}_n and \mathbf{d}_i , respectively, and similar notation is used hereafter. Comparing Eq. (3.4) with Eq. (3.24), vector potential in Eqs. (3.4) and (3.24) are different from each other by the choice of the gauge given by Eq. (3.24). Therefore, the eigen functions and eigenvalues of Eqs. (3.4) and (3.24) are related as

$$\psi_{\xi}^{a_i, 0}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i) = e^{-i\frac{e}{\hbar}\chi(\mathbf{r}, \mathbf{R}_n + \mathbf{d}_i)} \psi_{\xi}^{a_i, \mathbf{R}_n + \mathbf{d}_i}(\mathbf{r}) \quad (3.27)$$

and

$$\mathcal{E}_{\xi}^{a_i, 0} = \mathcal{E}_{\xi}^{a_i, \mathbf{R}_n + \mathbf{d}_i}, \quad (3.28)$$

respectively. In addition, by using Eqs. (3.14) and (3.27), we can immediately get

$$\Delta \mathcal{E}_{\xi}^{a_i, \mathbf{d}_i} = \Delta \mathcal{E}_{\xi}^{a_i, \mathbf{R}_n + \mathbf{d}_i}. \quad (3.29)$$

By using Eqs. (3.27), (3.28) and (3.29), the Hamiltonian matrix Eq. (3.22) is rewritten as

$$H_{\mathbf{R}_m j \eta, \mathbf{R}_n i \xi} = \left(\mathcal{E}_{\xi}^{a_i, 0} + \Delta \mathcal{E}_{\xi}^{a_i, \mathbf{d}_i} \right) \delta_{j,i} \delta_{\mathbf{R}_m, \mathbf{R}_n} \delta_{\eta, \xi} + \left(1 - \delta_{\mathbf{R}_m, \mathbf{R}_n} \delta_{j,i} \right) e^{-i\frac{eB}{\hbar}(R_{nx} + d_{ix} - R_{mx} - d_{jx})(R_{my} + d_{jy})} \\ \times T_{\eta \xi}^{a_j a_i}(\mathbf{R}_n - \mathbf{R}_m + \mathbf{d}_i - \mathbf{d}_j), \quad (3.30)$$

with

$$T_{\eta \xi}^{a_j a_i}(\mathbf{R}_n - \mathbf{R}_m + \mathbf{d}_i - \mathbf{d}_j) = \int \psi_{\eta}^{a_j, 0}(\mathbf{r})^{\dagger} \left(\frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_\ell - \mathbf{d}_i + \mathbf{d}_j)}{2} \right) \psi_{\xi}^{a_i, \mathbf{R}_\ell + \mathbf{d}_i - \mathbf{d}_j}(\mathbf{r}) d^3 r. \quad (3.31)$$

Hereafter, we refer to $T_{\eta \xi}^{a_j a_i}(\mathbf{R}_\ell + \mathbf{d}_i - \mathbf{d}_j)$ as the ‘magnetic hopping integral’. By using Eq. (3.27), we can derive the following property for the magnetic hopping integral:

$$T_{\xi \eta}^{a_i a_j}(-(\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j))^* = e^{i\frac{eB}{\hbar}(R_{nx} + d_{ix} - d_{jx})(R_{ny} + d_{iy} - d_{jy})} T_{\eta \xi}^{a_j a_i}(\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j). \quad (3.32)$$

This property is very important because it guarantees the hermicity of the Hamiltonian matrix Eq. (3.30). In the following section, we will approximate the magnetic hopping integral,

and then Eq. (3.32) may work as one of the criteria of whether the approximation is physically sound or not.

3.2 Approximation of the matrix elements

In order to calculate the Hamiltonian matrix Eq. (3.30), we need both $T_{\eta\xi}^{a_j a_i}(\mathbf{R}_\ell + \mathbf{d}_i - \mathbf{d}_j)$ and $\varepsilon_\xi^{a_i,0} + \Delta\varepsilon_\xi^{a_i,d_i}$. For this aim, we employ the perturbation theory, where the effect of the magnetic field is treated as the perturbation. This treatment enables us to calculate both $T_{\eta\xi}^{a_j a_i}(\mathbf{R}_\ell + \mathbf{d}_i - \mathbf{d}_j)$ and $\varepsilon_\xi^{a_i,0} + \Delta\varepsilon_\xi^{a_i,d_i}$ by utilizing the atomic spectrum and relativistic hopping integrals for zero magnetic field.

3.2.1 Approximation of $\varepsilon_\xi^{a_i,0} + \Delta\varepsilon_\xi^{a_i,d_i}$

Since $\varepsilon_\xi^{a_i,0}$ and $\Delta\varepsilon_\xi^{a_i,d_i}$ are independent of the choice of the gauge, we may use the symmetric gauge for simplicity in approximating $\varepsilon_\xi^{a_i,0} + \Delta\varepsilon_\xi^{a_i,d_i}$. In the symmetric gauge, the Dirac equation for an atom is obtained by replacing $\mathbf{A}(\mathbf{r})$ with $\mathbf{A}_{sym}(\mathbf{r})$ in Eq. (3.23), where $\mathbf{A}_{sym}(\mathbf{r})$ is the vector potential in the symmetric gauge and is given by $\mathbf{B} \times \mathbf{r} / 2$. This approximation would be valid because $\psi_\xi^{a_i,0}(\mathbf{r})$ has a large value in the vicinity of the origin, where the magnitude of $\mathbf{A}_{sym}(\mathbf{r})$ is small. The unperturbed wave function is given by $\varphi_{n\ell JM}^{a_i}(\mathbf{r})$, which is the eigen function of Eq. (2.6). Note that the unperturbed eigenvalue $\bar{\varepsilon}_{n\ell J}^{a_i}$ is $(2J+1)$ fold degenerate. In order to derive the first order perturbation energy, we shall consider the matrix elements of $ce\boldsymbol{\alpha} \cdot \mathbf{A}_{sym}(\mathbf{r})$ with respect to degenerate states $\varphi_{n\ell JM}^{a_i}(\mathbf{r})$ as follow:

Let us denote the Hamiltonian of the Dirac equation for an isolated atom at origin in the uniform magnetic field by following notations

$$H = H_o + H' \quad (3.33)$$

with

$$H_o = c\boldsymbol{\alpha} \cdot \mathbf{p} + \beta mc^2 + V_{a_i}(\mathbf{r}), \quad (3.34)$$

and

$$H' = ec\boldsymbol{\alpha} \cdot \mathbf{A}_{sym}(\mathbf{r}), \quad (3.35)$$

where H_o is the Dirac Hamiltonian in the absence of magnetic field (zero magnetic field). Then Dirac Eq. (3.23) becomes

$$(H_o + H')\psi_\xi^{a_i,0}(\mathbf{r})_{sym} = \varepsilon_\xi^{a_i,0}\psi_\xi^{a_i,0}(\mathbf{r})_{sym}, \quad (3.36)$$

where $\psi_{\xi}^{a_i,0}(\mathbf{r})_{sym}$ denotes the eigen function in the case of the symmetric gauge. Since $\psi_{\xi}^{a_i,0}(\mathbf{r})_{sym}$ may have the large value in the vicinity of the origin while $|\mathbf{A}_{sym}(\mathbf{r})|$ is small, we can deal with H' as a perturbation and H_o as unperturbed Hamiltonian. The Dirac equation for unperturbed Hamiltonian is same as the Eq. (2.6) that is given by

$$H_o \varphi_{n\ell JM}^{a_i}(\mathbf{r}) = \bar{\varepsilon}_{n\ell J}^{a_i} \varphi_{n\ell JM}^{a_i}(\mathbf{r}). \quad (3.37)$$

Note that the unperturbed eigenvalue $\bar{\varepsilon}_{n\ell J}^{a_i}$ is $(2J+1)$ -fold degenerate. According to perturbation theory, we have to consider the following matrix,

$$H'_{n\ell JM', n\ell JM} = \int \varphi_{n\ell JM'}^{a_i}(\mathbf{r})^\dagger H' \varphi_{n\ell JM}^{a_i}(\mathbf{r}) d^3 r. \quad (3.38)$$

If we express, $\varepsilon_{\xi}^{a_i,0} = \bar{\varepsilon}_{n\ell J}^{a_i} + \varepsilon^1 + \varepsilon^2 + \dots$, then the first order correction term ε^1 , which is linear with H' , can be obtained as the eigenvalues of $H'_{n\ell JM', n\ell JM}$. Substituting Eq. (3.35) into Eq. (3.38), we have

$$H'_{n\ell JM', n\ell JM} = \int \varphi_{n\ell JM'}^{a_i}(\mathbf{r})^\dagger \{ec\alpha \cdot \mathbf{A}_{sym}(\mathbf{r})\} \varphi_{n\ell JM}^{a_i}(\mathbf{r}) d^3 r \quad (3.39)$$

Here, let us denote the large and small component of $\varphi_{n\ell JM}^{a_i}(\mathbf{r})$ by $f_{n\ell JM}^{a_i}(\mathbf{r})$ and $g_{n\ell JM}^{a_i}(\mathbf{r})$, respectively, i.e., we have

$$\varphi_{n\ell JM}^{a_i}(\mathbf{r}) = \begin{pmatrix} f_{n\ell JM}^{a_i}(\mathbf{r}) \\ g_{n\ell JM}^{a_i}(\mathbf{r}) \end{pmatrix}. \quad (3.40)$$

And we know that

$$\alpha_x = \begin{pmatrix} 0 & \sigma_x \\ \sigma_x & 0 \end{pmatrix}, \quad \alpha_y = \begin{pmatrix} 0 & \sigma_y \\ \sigma_y & 0 \end{pmatrix}, \quad \alpha_z = \begin{pmatrix} \sigma_z & 0 \\ 0 & \sigma_z \end{pmatrix}. \quad (3.41)$$

From Eqs. (3.39), (3.40) and (3.41), we have

$$H'_{n\ell JM', n\ell JM} = ce \int \left\{ f_{n\ell JM'}^{a_i}(\mathbf{r})^\dagger \{ \mathbf{A}_{sym}(\mathbf{r}) \cdot \boldsymbol{\sigma} \} g_{n\ell JM}^{a_i}(\mathbf{r}) + g_{n\ell JM'}^{a_i}(\mathbf{r})^\dagger \{ \mathbf{A}_{sym}(\mathbf{r}) \cdot \boldsymbol{\sigma} \} f_{n\ell JM}^{a_i}(\mathbf{r}) \right\} d^3 r \quad (3.42)$$

where we used the property $\mathbf{A}(\mathbf{r}) \cdot \boldsymbol{\sigma} = \boldsymbol{\sigma} \cdot \mathbf{A}(\mathbf{r})$.

In order to evaluate the above matrix element Eq. (3.42), we introduce an approximation [39],

$$g_{n\ell JM}^{a_i}(\mathbf{r}) \approx \frac{1}{2mc} \boldsymbol{\sigma} \cdot \mathbf{p} f_{n\ell JM}^{a_i}(\mathbf{r}). \quad (3.43)$$

Taking the first term of Eq. (3.42) and substituting Eq. (3.43), we have

$$ce \int f_{n\ell JM'}^{a_i}(\mathbf{r})^\dagger \{A_{sym}(\mathbf{r}) \cdot \sigma\} g_{n\ell JM}^{a_i}(\mathbf{r}) d^3 r \approx \frac{ce}{2mc} \int f_{n\ell JM'}^{a_i}(\mathbf{r})^\dagger \{A(\mathbf{r}) \cdot \sigma\} \{\mathbf{p} \cdot \sigma\} f_{n\ell JM}^{a_i}(\mathbf{r}) d^3 r.$$

Using the property $A_{sym}(\mathbf{r}) \cdot \sigma = \sigma \cdot A_{sym}(\mathbf{r})$ and $\mathbf{p} \cdot \sigma = \sigma \cdot \mathbf{p}$, then we have

$$ce \int f_{n\ell JM'}^{a_i}(\mathbf{r})^\dagger \{A_{sym}(\mathbf{r}) \cdot \sigma\} g_{n\ell JM}^{a_i}(\mathbf{r}) d^3 r \approx \frac{e}{2m} \int f_{n\ell JM'}^{a_i}(\mathbf{r})^\dagger \{\sigma \cdot A_{sym}(\mathbf{r})\} \{\sigma \cdot \mathbf{p}\} f_{n\ell JM}^{a_i}(\mathbf{r}) d^3 r.$$

Again using the property, $\sigma \cdot \mathbf{C} + \sigma \cdot \mathbf{D} = \mathbf{C} \cdot \mathbf{D} + i\sigma \cdot \mathbf{C} \times \mathbf{D}$, then the above equation becomes

$$ce \int f_{n\ell JM'}^{a_i}(\mathbf{r})^\dagger \{A_{sym}(\mathbf{r}) \cdot \sigma\} g_{n\ell JM}^{a_i}(\mathbf{r}) d^3 r \approx \frac{e}{2m} \int f_{n\ell JM'}^{a_i}(\mathbf{r})^\dagger [\{A_{sym}(\mathbf{r}) \cdot \mathbf{p} + i\sigma \cdot A_{sym}(\mathbf{r}) \times \mathbf{p}\}] f_{n\ell JM}^{a_i}(\mathbf{r}) d^3 r. \quad (3.44)$$

Taking second term of Eq. (3.42), we have

$$ce \int g_{n\ell JM'}^{a_i}(\mathbf{r})^\dagger \{A_{sym}(\mathbf{r}) \cdot \sigma\} f_{n\ell JM}^{a_i}(\mathbf{r}) d^3 r = ce \int [\{\sigma \cdot A_{sym}(\mathbf{r})\} g_{n\ell JM'}^{a_i}(\mathbf{r})]^\dagger f_{n\ell JM}^{a_i}(\mathbf{r}) d^3 r. \quad (3.45)$$

Substituting Eq. (3.43) into Eq. (3.45), we have

$$\begin{aligned} ce \int g_{n\ell JM'}^{a_i}(\mathbf{r})^\dagger \{A_{sym}(\mathbf{r}) \cdot \sigma\} f_{n\ell JM}^{a_i}(\mathbf{r}) d^3 r \\ = \frac{e}{2m} \int [\{\sigma \cdot A_{sym}(\mathbf{r})\} \{\mathbf{p} \cdot \sigma\} f_{n\ell JM'}^{a_i}(\mathbf{r})]^\dagger f_{n\ell JM}^{a_i}(\mathbf{r}) d^3 r \\ = \frac{e}{2m} \int f_{n\ell JM'}^{a_i}(\mathbf{r})^\dagger [\{\sigma \cdot \mathbf{p}\} \{\sigma \cdot A_{sym}(\mathbf{r})\}] f_{n\ell JM}^{a_i}(\mathbf{r}) d^3 r. \end{aligned}$$

Using property $\sigma \cdot \mathbf{C} + \sigma \cdot \mathbf{D} = \mathbf{C} \cdot \mathbf{D} + i\sigma \cdot \mathbf{C} \times \mathbf{D}$ again, we have

$$\begin{aligned} ce \int g_{n\ell JM'}^{a_i}(\mathbf{r})^\dagger \{A_{sym}(\mathbf{r}) \cdot \sigma\} f_{n\ell JM}^{a_i}(\mathbf{r}) d^3 r = \frac{e}{2m} \int f_{n\ell JM'}^{a_i}(\mathbf{r})^\dagger [\mathbf{p} \cdot A_{sym}(\mathbf{r}) + i\sigma \cdot \{\mathbf{p} \times A_{sym}(\mathbf{r})\}] \\ \times f_{n\ell JM}^{a_i}(\mathbf{r}) d^3 r. \end{aligned} \quad (3.46)$$

Now, substituting Eqs. (3.44) and (3.46) into Eq. (3.42), we get

$$\begin{aligned} H'_{n\ell JM', n\ell JM} \approx \frac{e}{2m} \int f_{n\ell JM'}^{a_i}(\mathbf{r})^\dagger [\mathbf{p} \cdot A_{sym}(\mathbf{r}) + A_{sym}(\mathbf{r}) \cdot \mathbf{p}] f_{n\ell JM}^{a_i}(\mathbf{r}) d^3 r \\ + \frac{ie}{2m} \int f_{n\ell JM'}^{a_i}(\mathbf{r})^\dagger [\sigma \cdot \{\mathbf{p} \times A_{sym}(\mathbf{r})\} + A_{sym}(\mathbf{r}) \times \mathbf{p}] f_{n\ell JM}^{a_i}(\mathbf{r}) d^3 r \end{aligned} \quad (3.47)$$

Let us first calculate the first term of Eq. (3.47). Since, $\nabla \cdot A_{sym}(\mathbf{r}) = 0$, then we get

$$\{\mathbf{p} \cdot \mathbf{A}_{\text{sym}}(\mathbf{r}) + \mathbf{A}_{\text{sym}}(\mathbf{r}) \cdot \mathbf{p}\} f_{n\ell JM}^{a_i}(\mathbf{r}) = \frac{2\hbar}{i} \mathbf{A}_{\text{sym}}(\mathbf{r}) \cdot \nabla f_{n\ell JM}^{a_i}(\mathbf{r}) \quad (3.48)$$

Similarly, the second term of Eq. (3.47), is written as

$$\begin{aligned} \{\mathbf{p} \times \mathbf{A}_{\text{sym}}(\mathbf{r}) + \mathbf{A}_{\text{sym}}(\mathbf{r}) \times \mathbf{p}\} f_{n\ell JM}^{a_i}(\mathbf{r}) &= \frac{\hbar}{i} [\nabla \times \{\mathbf{A}_{\text{sym}}(\mathbf{r}) f_{n\ell JM}^{a_i}(\mathbf{r})\} + \mathbf{A}_{\text{sym}}(\mathbf{r}) \times \nabla f_{n\ell JM}^{a_i}(\mathbf{r})] \\ &= \frac{\hbar}{i} [\nabla \times \{\mathbf{A}_{\text{sym}}(\mathbf{r}) f_{n\ell JM}^{a_i}(\mathbf{r})\} + \mathbf{A}_{\text{sym}}(\mathbf{r}) \times \nabla f_{n\ell JM}^{a_i}(\mathbf{r})] \\ &= \frac{\hbar}{i} [\nabla \times \{\mathbf{A}_{\text{sym}}(\mathbf{r}) f_{n\ell JM}^{a_i}(\mathbf{r})\} + \mathbf{A}_{\text{sym}}(\mathbf{r}) \times \nabla f_{n\ell JM}^{a_i}(\mathbf{r})] \\ &= \frac{\hbar}{i} [-\mathbf{A}_{\text{sym}}(\mathbf{r}) \times \nabla f_{n\ell JM}^{a_i}(\mathbf{r}) + f_{n\ell JM}^{a_i}(\mathbf{r}) \nabla \times \mathbf{A}_{\text{sym}}(\mathbf{r}) \\ &\quad + \mathbf{A}_{\text{sym}}(\mathbf{r}) \times \nabla f_{n\ell JM}^{a_i}(\mathbf{r})] \\ &= \frac{\hbar}{i} f_{n\ell JM}^{a_i}(\mathbf{r}) \mathbf{B}. \quad (\cdot : \mathbf{B} = \nabla \times \mathbf{A}(\mathbf{r})) \end{aligned} \quad (3.49)$$

Hence, Eq. (3.47) becomes

$$H'_{n\ell JM', n\ell JM} \approx \frac{e}{m} \int f_{n\ell JM'}^{a_i}(\mathbf{r})^\dagger \{\mathbf{A}_{\text{sym}}(\mathbf{r}) \cdot \mathbf{p}\} f_{n\ell JM}^{a_i}(\mathbf{r}) d^3 r + \frac{e\hbar}{2m} \int f_{n\ell JM'}^{a_i}(\mathbf{r})^\dagger \{\boldsymbol{\sigma} \cdot \mathbf{B}\} \\ \times f_{n\ell JM}^{a_i}(\mathbf{r}) d^3 r. \quad (3.50)$$

Taking the first part of Eq. (3.50), we have

$$\begin{aligned} \frac{e}{m} \int f_{n\ell JM'}^{a_i}(\mathbf{r})^\dagger \{\mathbf{A}_{\text{sym}}(\mathbf{r}) \cdot \mathbf{p}\} f_{n\ell JM}^{a_i}(\mathbf{r}) d^3 r &= \frac{e}{m} \int f_{n\ell JM'}^{a_i}(\mathbf{r})^\dagger \left\{ \left(\frac{1}{2} \mathbf{B} \times \mathbf{r} \right) \cdot \mathbf{p} \right\} f_{n\ell JM}^{a_i}(\mathbf{r}) d^3 r \\ &= \frac{e}{m} \int f_{n\ell JM'}^{a_i}(\mathbf{r})^\dagger \left\{ \left(\frac{1}{2} \mathbf{B} \times \mathbf{r} \right) \cdot \mathbf{p} \right\} f_{n\ell JM}^{a_i}(\mathbf{r}) d^3 r \\ &= \frac{e}{2m} \int f_{n\ell JM'}^{a_i}(\mathbf{r})^\dagger \mathbf{B} \cdot \{\mathbf{r} \times \mathbf{p} f_{n\ell JM}^{a_i}(\mathbf{r})\} d^3 r \\ &= \frac{e}{2m} \int f_{n\ell JM'}^{a_i}(\mathbf{r})^\dagger (\mathbf{B} \cdot \mathbf{l}) f_{n\ell JM}^{a_i}(\mathbf{r}) d^3 r \end{aligned} \quad (3.51)$$

Substituting Eq. (3.51) into Eq. (3.50), we finally get

$$H'_{n\ell JM', n\ell JM} = \frac{e}{2m} \int f_{n\ell JM'}^{a_i}(\mathbf{r})^\dagger \{\mathbf{B} \cdot (\mathbf{l} + 2\mathbf{S})\} f_{n\ell JM}^{a_i}(\mathbf{r}) d^3 r, \quad (3.52)$$

where $\mathbf{s} = \frac{\hbar}{2} \boldsymbol{\sigma}$.

Next, we shall calculate the RHS of Eq. (3.52) by substituting the specific form of $f_{n\ell JM}^{a_i}(\mathbf{r})$

that is given by $F_{n\ell JM}^{a_i}(\mathbf{r})y_{\ell,J}^M(\theta, \phi)/r$ (see, Eq. (2.6) in Chapter 2). Recalling that $y_{\ell,J}^M(\theta, \phi)$ is given by

$$y_{\ell J}^M(\theta, \phi) = \begin{cases} \begin{pmatrix} \sqrt{\frac{J+M}{2J}} Y_{\ell, M-\frac{1}{2}}(\theta, \phi) \\ \sqrt{\frac{J-M}{2J}} Y_{\ell, M+\frac{1}{2}}(\theta, \phi) \end{pmatrix} & (\text{for } J = \ell + \frac{1}{2}) \\ \begin{pmatrix} -\sqrt{\frac{J+1-M}{2(J+1)}} Y_{\ell, M-\frac{1}{2}}(\theta, \phi) \\ \sqrt{\frac{J+1+M}{2(J+1)}} Y_{\ell, M+\frac{1}{2}}(\theta, \phi) \end{pmatrix} & (\text{for } J = \ell - \frac{1}{2}) \end{cases}, \quad (3.53)$$

then we get

$$H'_{n\ell JM', n\ell JM} \approx \frac{eB}{2m} \frac{2J+1}{2\ell+1} \hbar M \delta_{M, M'}, \quad (3.54)$$

for both cases $J = \ell + \frac{1}{2}$ and $J = \ell - \frac{1}{2}$. In this derivation, we used the approximation

$$\int \frac{1}{r^2} |f_{n\ell J}^{a_i}(\mathbf{r})| d^3r = 1. \quad (3.55)$$

From Eq. (3.54), we can say that $H_{n\ell JM \square n\ell JM}^{\square}$ is the diagonal matrix and energy eigenvalue is given by

$$\varepsilon^1 = \frac{eB}{2m} \frac{2J+1}{2\ell+1} \hbar M. \quad (3.56)$$

Thus, we finally get

$$\varepsilon_{\xi}^{a_i, 0} = \bar{\varepsilon}_{n\ell J}^{a_i} + \frac{eB}{2m} \left(\frac{2J+1}{2\ell+1} \right) \hbar M \quad (3.57)$$

Next, let us consider the approximation of $\Delta \varepsilon_{\xi}^{a_i, d_i}$. As mentioned before, $\psi_{\xi}^{a_i, 0}(\mathbf{r})$ would be well localized in the vicinity of the origin, and the magnitude of $A_{\text{sym}}(\mathbf{r})$ is small around there. Therefore, it would be reasonable that the relativistic atomic orbital in the uniform magnetic field, $\psi_{\xi}^{a_i, 0}(\mathbf{r})_{\text{sym}}$ is approximated as the unperturbed wave function that fits onto the perturbation (zeroth order wave function). From Eq. (3.54), we have

$$\psi_{\xi}^{a_i, 0}(\mathbf{r})_{\text{sym}} \approx \varphi_{n\ell JM}^{a_i}(\mathbf{r}). \quad (3.58)$$

By using Eqs. (3.14) and (3.58), it is also found that $\Delta \varepsilon_{\xi}^{a_i, d_i}$ is approximated by

$$\Delta \mathcal{E}_\xi^{a_i, d_i} = \int \varphi_{n\ell JM}^{a_i}(\mathbf{r} - \mathbf{d}_i)^\dagger \left\{ \sum_{\substack{\mathbf{R}_m \\ (\mathbf{R}_m + \mathbf{d}_k \neq \mathbf{d}_i)}} \sum_k V_{a_k}(\mathbf{r} - \mathbf{R}_m - \mathbf{d}_k) \right\} \varphi_{n\ell JM}^{a_i}(\mathbf{r} - \mathbf{d}_i) d^3 r. \quad (3.59)$$

Equation (3.59) is the energy of the crystal field, which is identical with $\Delta \bar{\mathcal{E}}_{n\ell J}^{a_i, d_i}$ from Eq. (2.17). Using Eqs. (2.17), (3.57) and (3.59), $\mathcal{E}_\xi^{a_i, 0} + \Delta \mathcal{E}_\xi^{a_i, d_i}$ is thus approximated by

$$\mathcal{E}_\xi^{a_i, 0} + \Delta \mathcal{E}_\xi^{a_i, d_i} \approx \bar{\mathcal{E}}_{n\ell J}^{a_i} + \Delta \bar{\mathcal{E}}_{n\ell JM}^{a_i, d_i} + \frac{eB}{2m} \left(\frac{2J+1}{2\ell+1} \right) \hbar M. \quad (3.60)$$

3.2.2 Approximation of $T_{\eta\xi}^{a_j a_i}(\mathbf{R}_\ell + \mathbf{d}_i - \mathbf{d}_j)$

In order to evaluate $T_{\eta\xi}^{a_j a_i}(\mathbf{R}_\ell + \mathbf{d}_i - \mathbf{d}_j)$ given by Eq. (3.31), we approximate both $\psi_\eta^{a_j, 0}(\mathbf{r})$ and $\psi_\xi^{a_i, \mathbf{R}_\ell + \mathbf{d}_i - \mathbf{d}_j}(\mathbf{r})$ by means of the lowest order perturbation theory for degenerate states. Note that both $\psi_\eta^{a_j, 0}(\mathbf{r})$ and $\psi_\xi^{a_i, \mathbf{R}_\ell + \mathbf{d}_i - \mathbf{d}_j}(\mathbf{r})$ in Eq. (3.31) are the wave functions of the Landau gauge. In general, the wave function of the Landau gauge can be obtained from that of the symmetric gauge through the following transformation:

$$\psi_\eta^{a_j, 0}(\mathbf{r}) = e^{-i\frac{e}{2\hbar}Bxy} \psi_\eta^{a_j, 0}(\mathbf{r})_{sym}, \quad (3.61)$$

$$\psi_\xi^{a_i, \mathbf{R}_\ell + \mathbf{d}_i - \mathbf{d}_j}(\mathbf{r}) = e^{-i\frac{e}{2\hbar}Bxy} \psi_\xi^{a_i, \mathbf{R}_\ell + \mathbf{d}_i - \mathbf{d}_j}(\mathbf{r})_{sym}, \quad (3.62)$$

where $Bxy/2$ denotes the gauge transformation function from the symmetric gauge to the Landau gauge. Using Eqs. (3.58) and (3.61), $\psi_\eta^{a_j, 0}(\mathbf{r})$ of the Landau gauge is approximately given by

$$\psi_\eta^{a_j, 0}(\mathbf{r}) \approx e^{-i\frac{e}{2\hbar}Bxy} \varphi_{n'\ell'JM'}^{a_j}(\mathbf{r}), \quad (3.63)$$

where $\varphi_{n'\ell'JM'}^{a_j}(\mathbf{r})$ is the zeroth order wave function for $\psi_\eta^{a_j, 0}(\mathbf{r})_{sym}$. Furthermore, since $\varphi_{n'\ell'JM'}^{a_j}(\mathbf{r})$ is localized around the origin, the phase factor $\exp(-ieBxy/2\hbar)$ would be approximated by 1, near the origin where the magnitude of $\varphi_{n'\ell'JM'}^{a_j}(\mathbf{r})$ is not negligibly small. Thus, we shall approximate Eq. (3.63) as

$$\psi_\eta^{a_j, 0}(\mathbf{r}) \approx \varphi_{n'\ell'JM'}^{a_j}(\mathbf{r}). \quad (3.64)$$

Similar to Eq. (3.27), in the case of symmetric gauge, $\psi_\xi^{a_i, \mathbf{R}_\ell + \mathbf{d}_i - \mathbf{d}_j}(\mathbf{r})_{sym}$ is related to $\psi_\xi^{a_i, 0}(\mathbf{r} - \mathbf{R}_\ell - \mathbf{d}_i + \mathbf{d}_j)_{sym}$ by

$$\psi_{\xi}^{a_i,0}(\mathbf{r}-\mathbf{R}_{\ell}-\mathbf{d}_i+\mathbf{d}_j)_{sym} = e^{-\frac{eB}{2\hbar}\{(R_{ly}+d_{ly}-d_{jy})x-(R_{lx}+d_{lx}-d_{jx})y\}} \psi_{\xi}^{a_i,\mathbf{R}_{\ell}+\mathbf{d}_i-\mathbf{d}_j}(\mathbf{r})_{sym} \quad (3.65)$$

where we use $\chi(\mathbf{r}, \mathbf{R}_{\ell} + \mathbf{d}_i - \mathbf{d}_j) = B\{(R_{ly} + d_{ly} - d_{jy})x - (R_{lx} + d_{lx} - d_{jx})y\} / 2$ for the symmetric gauge. Using Eqs. (3.62) and (3.65), we gave

$$\begin{aligned} \psi_{\xi}^{a_i,\mathbf{R}_{\ell}+\mathbf{d}_i-\mathbf{d}_j}(\mathbf{r}) &= e^{-i\frac{e}{2\hbar}Bxy} \psi_{\xi}^{a_i,\mathbf{R}_{\ell}+\mathbf{d}_i-\mathbf{d}_j}(\mathbf{r})_{sym} \\ &= e^{-i\frac{eB}{2\hbar}\{(R_{ly}+d_{ly}-d_{jy})x-(R_{lx}+d_{lx}-d_{jx})y+xy\}} \psi_{\xi}^{a_i,0}(\mathbf{r}-\mathbf{R}_{\ell}-\mathbf{d}_i+\mathbf{d}_j)_{sym}. \end{aligned} \quad (3.66)$$

Since $\psi_{\xi}^{a_i,0}(\mathbf{r}-\mathbf{R}_{\ell}-\mathbf{d}_i+\mathbf{d}_j)_{sym}$ is localized around $\mathbf{r} = \mathbf{R}_{\ell} + \mathbf{d}_i - \mathbf{d}_j$, the phase factor $\exp[-ieB\{(R_{ly} + d_{ly} - d_{jy})x - (R_{lx} + d_{lx} - d_{jx})y + xy\} / 2\hbar]$ would be approximated by the phase factor at $\mathbf{r} = \mathbf{R}_{\ell} + \mathbf{d}_i - \mathbf{d}_j$. Furthermore using Eq. (3.58), we finally get

$$\psi_{\xi}^{a_i,\mathbf{R}_{\ell}+\mathbf{d}_i-\mathbf{d}_j}(\mathbf{r}) \approx e^{-i\frac{eB}{2\hbar}(R_{ly}+d_{ly}-d_{jy})(R_{lx}+d_{lx}-d_{jx})} \phi_{n\ell JM}^{a_i}(\mathbf{r}-\mathbf{R}_{\ell}-\mathbf{d}_i+\mathbf{d}_j). \quad (3.67)$$

Substituting Eqs. (3.64) and (3.67) into Eq. (3.31), we obtain the approximate form of $T_{\eta\xi}^{a_j a_i}(\mathbf{R}_{\ell} + \mathbf{d}_i - \mathbf{d}_j)$:

$$T_{\eta\xi}^{a_j a_i}(\mathbf{R}_{\ell} + \mathbf{d}_i - \mathbf{d}_j) \approx e^{-i\frac{eB}{2\hbar}(R_{ly}+d_{ly}-d_{jy})(R_{lx}+d_{lx}-d_{jx})} t_{n'\ell'JM',n\ell JM}^{a_j a_i}(\mathbf{R}_{\ell} + \mathbf{d}_i - \mathbf{d}_j), \quad (3.68)$$

where $t_{n'\ell'JM',n\ell JM}^{a_j a_i}(\mathbf{R}_{\ell} + \mathbf{d}_i - \mathbf{d}_j)$ is the relativistic hopping integral for zero magnetic field, and is defined by Eq. (2.21). In this approximation, the effect of the magnetic field is stuffed into the phase factor $\exp\{-ieB(R_{lx} + d_{lx} - d_{jx})(R_{ly} + d_{ly} - d_{jy}) / 2\hbar\}$. Equation (3.68) is just identical with the approximation using Peierls phase [9,13]. That is to say, the Peierls phase is revisited by the lowest order approximation of the perturbation theory. This means that not only the validity of using the Peierls phase is confirmed [9,13], but also symmetrical improvements beyond Eq. (3.68) would also be possible by incorporating the higher order corrections of the perturbation theory into Eq. (3.58).

Concerning Eq. (3.68), we also emphasize that the Hamiltonian matrix with the use of Eq. (3.68) remains to be a Hermitian matrix as it should be. This is easily confirmed by the fact that Eq. (3.68) satisfies Eq. (3.32). Substituting Eqs. (3.60) and (3.68) into Eq. (3.30), leads to

$$\begin{aligned} H_{\mathbf{R}_m j(n'\ell'JM'), \mathbf{R}_n i(n\ell JM)} &= \left\{ \bar{\varepsilon}_{n\ell J}^{a_i}(\mathbf{B}=0) + \Delta \bar{\varepsilon}_{n\ell JM}^{a_i, \mathbf{d}_i}(\mathbf{B}=0) + \frac{eB}{2m} \left(\frac{2J+1}{2\ell+1} \right) \hbar M \right\} \delta_{\mathbf{R}_m, \mathbf{R}_n} \delta_{j,i} \\ &\times \delta_{n'\ell'JM', i n \ell JM} + (1 - \delta_{j,i} \delta_{\mathbf{R}_m, \mathbf{R}_n}) e^{-i\frac{eB}{2\hbar}(R_{nx}+d_{ix}-R_{mx}-d_{jx})(R_{ny}+d_{iy}+R_{my}+d_{jy})} \\ &\times t_{n'\ell'JM',n\ell JM}^{a_j a_i}(\mathbf{R}_n - \mathbf{R}_m + \mathbf{d}_i - \mathbf{d}_j). \end{aligned} \quad (3.69)$$

The effects of the magnetic field are included both in the diagonal elements [the first term of Eq. (3.69)] as the Zeeman term and in the off-diagonal elements as the phase factor $\exp\{-ieB(R_{lx} + d_{ix} - d_{jx})(R_{ly} + d_{ly} - d_{jy})/2\hbar\}$. It is also found from Eq. (3.69) that relativistic effects are included both in $\overline{t}_{n\ell J}^{a_i} + \square\overline{t}_{n\ell JM}^{a_i, d_i}$ and in the relativistic hopping integral $t_{n'\ell'JM', n\ell JM}^{a_j a_i}(\mathbf{R}_n - \mathbf{R}_m + \mathbf{d}_i - \mathbf{d}_j)$. Substituting Eq. (3.69) into Eq. (3.7), and rewrite \square and \square by (n', ℓ', J', M') and (n, ℓ, J, M) respectively, the simultaneous equations for the expansion coefficients are given by

$$\begin{aligned} & \left\{ \overline{\varepsilon}_{n'\ell'J'}^{a_j} + \Delta \varepsilon_{n'\ell'JM'}^{-a_j, \mathbf{d}_j} + \frac{eB}{2m} \left(\frac{2J'+1}{2\ell'+1} \right) \hbar M' \right\} C_k^{n'\ell'JM'}(\mathbf{R}_m + \mathbf{d}_j) + \sum_{n\ell JM} \sum_{\mathbf{R}_n} \sum_i (1 - \delta_{j,i} \delta_{\mathbf{R}_m, \mathbf{R}_n}) \\ & \times e^{-i\frac{eB}{2\hbar}(R_{nx} + d_{ix} - R_{mx} - d_{jx})(R_{ny} + d_{ly} + R_{my} + d_{jy})} t_{n'\ell'JM', n\ell JM}^{a_j a_i}(\mathbf{R}_n - \mathbf{R}_m + \mathbf{d}_i - \mathbf{d}_j) C_k^{n\ell JM}(\mathbf{R}_n + \mathbf{d}_i) \\ & = E_k C_k^{n'\ell'JM'}(\mathbf{R}_m + \mathbf{d}_j). \end{aligned} \quad (3.70)$$

Finally, we rewrite Eq. (3.70) in a convenient form. Equation (3.70) can be rewritten by replacing the sums with respect to \mathbf{R}_n and i by the sum with respect to the vectors connecting the atom located at $\mathbf{R}_m + \mathbf{d}_j$ to its neighboring atoms. Since such vectors are independent of \mathbf{R}_m but depend on \mathbf{d}_j , they are denoted as $\mathbf{T}_W(\mathbf{d}_j)$ ($W = 1, 2, 3, \dots$). Here, W is numbered in the following order: $W = 1, 2, 3, \dots, W_1$ for the nearest neighbor atoms, $W = W_1 + 1, W_1 + 2, \dots, W_1 + W_2$ for the second nearest neighbor atoms, $W = W_2 + 1, W_2 + 2, \dots, W_1 + W_2 + W_3$ for the third nearest neighbor atoms, and so on. Note that, since $\mathbf{T}_W(\mathbf{d}_j)$ also denotes the vector connecting a_j atom to a_i atom, a_i varies with W . If we denote the dependence of a_i on W by $A(W)$, then Eq. (3.70) is rewritten as

$$\begin{aligned} & \left\{ \overline{\varepsilon}_{n'\ell'J'}^{a_j} + \Delta \varepsilon_{n'\ell'JM'}^{-a_j, \mathbf{d}_j} + \frac{eB}{2m} \left(\frac{2J'+1}{2\ell'+1} \right) \hbar M' \right\} C_k^{n'\ell'JM'}(\mathbf{R}_m + \mathbf{d}_j) + \sum_{n\ell JM} \sum_W e^{-i\frac{eB}{2\hbar} \mathbf{T}_{Wx}(\mathbf{d}_j) \{ \mathbf{T}_{Wy}(\mathbf{d}_j) + 2\mathbf{R}_{my} + 2d_{jy} \}} \\ & \times t_{n'\ell'JM', n\ell JM}^{a_j A(W)}(\mathbf{T}_W(\mathbf{d}_j)) C_k^{n\ell JM}(\mathbf{T}_W(\mathbf{d}_j) + \mathbf{R}_m + \mathbf{d}_j) = E_k C_k^{n'\ell'JM'}(\mathbf{R}_m + \mathbf{d}_j). \end{aligned} \quad (3.71)$$

Equation (3.71) is the resultant simultaneous equation to be solved. Although we can obtain the coefficients $C_k^{n\ell JM}(\mathbf{R}_n + \mathbf{d}_i)$ and E_k by solving the simultaneous equation [Eq. (3.71)], there are two problems in performing actual calculations. One is that we need the numerical values of $t_{n'\ell'JM', n\ell JM}^{a_j A(W)}(\mathbf{T}_W(\mathbf{d}_j))$. In Chapter 2, we have already presented the relativistic Slater-Koster table that enables us to calculate $t_{n'\ell'JM', n\ell JM}^{a_j A(W)}(\mathbf{T}_W(\mathbf{d}_j))$. As in Chapter 2, using the relativistic Slater-Koster table, the relativistic hopping integral $t_{n'\ell'JM', n\ell JM}^{a_j A(W)}(\mathbf{T}_W(\mathbf{d}_j))$ is expressed in terms of several TB parameters. TB parameters can be determined by requiring them to reproduce the electronic structure for zero magnetic field (as already mentioned in Chapter 2). Another problem is that we have to solve the simultaneous equation with an infinite number of expansion coefficients. In order to overcome this problem, we employ the

knowledge obtained from the transitional symmetry, i.e., magnetic Bloch theorem. In Chapters 4 and 5, we have shown the specific examples that Eq. (3.71) is reduced to the simultaneous equation with a finite number of coefficients with the aid of the magnetic Bloch theorem.

Chapter 4

Application to two-dimensional square lattice immersed in the uniform magnetic field

In this chapter, we apply the MFRTB method to the two-dimensional square lattice [Fig. 4.1] immersed in the uniform magnetic field. It is shown that Eq. (3.71) is reduced to the simultaneous equation with a finite number of expansion coefficients via the magnetic Bloch theorem.

The purpose of dealing with this system is to check the validity of the MFRTB method, and to confirm the benefits of treating the relativistic effects, because this system was previously calculated with the non-relativistic TB method by Hofstadter [8] and the result is well known [8].

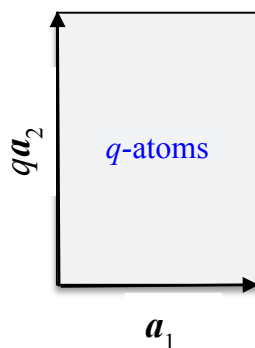


Fig. 4.1 Two-dimensional square lattice immersed in the uniform magnetic field.

4.1 Magnetic Bloch theorem

Let us consider the two-dimensional square lattice with lattice constant a . We suppose that atoms have only s -electrons ($\ell = 0$) and are located at each lattice points. The lattice vectors of the two-dimensional square lattice are given by

$$\mathbf{R}_n = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2, \quad (4.1)$$

where n_1 and n_2 are integers, and $\mathbf{a}_1 = a\mathbf{e}_x$ and $\mathbf{a}_2 = a\mathbf{e}_y$. The magnetic field is directed along the z -axis, and its magnitude B is supposed to be expressed by

$$B = \frac{2\pi\hbar}{ea^2} \frac{p}{q}, \quad (4.2)$$

where p and q are relatively prime integers [8,41,42].

In order to derive the magnetic Bloch theorem, let us consider the set of magnetic translation operators that commute with each other. The magnetic translation operator $U(\mathbf{R}_n)$ is defined as

$$U(\mathbf{R}_n) = e^{i\frac{e}{\hbar}\chi(\mathbf{r}, \mathbf{R}_n)} T(\mathbf{R}_n), \quad (4.3)$$

where $T(\mathbf{R}_n)$ denotes the usual translation operator given by $\exp(-i\mathbf{R}_n \cdot \mathbf{p} / \hbar)$ [44], and where $\chi(\mathbf{r}, \mathbf{R})$ is defined as the gauge transformation function, i.e.,

$$\mathbf{A}(\mathbf{r} - \mathbf{R}_n) = \mathbf{A}(\mathbf{r}) + \nabla\chi(\mathbf{r}, \mathbf{R}_n). \quad (4.4)$$

In the case of Landau gauge [Eq. (3.3)], $\chi(\mathbf{r}, \mathbf{R})$ is given by

$$\chi(\mathbf{r}, \mathbf{R}) = -BR_{nx}y. \quad (4.5)$$

The detailed derivation of $U(\mathbf{R}_n)$ is given in Appendix C. As shown in Appendix C, $U(\mathbf{R}_n)$ commutes with the Hamiltonian [Eq. (3.2)], i.e.,

$$[H, U(\mathbf{R}_n)] = 0. \quad (4.6)$$

The multiplication of $U(\mathbf{R}_n)$ and $U(\mathbf{R}_m)$ leads to

$$U(\mathbf{R}_n)U(\mathbf{R}_m) = e^{i\frac{e}{\hbar}\{\chi(\mathbf{r}, \mathbf{R}_n) + \chi(\mathbf{r} - \mathbf{R}_n, \mathbf{R}_m) - \chi(\mathbf{r}, \mathbf{R}_n + \mathbf{R}_m)\}} U(\mathbf{R}_n + \mathbf{R}_m) \quad (4.7)$$

Using Eq. (4.4)

$$U(\mathbf{R}_n)U(\mathbf{R}_m) = e^{-2\pi i \frac{p}{q} m_1 n_2} U(\mathbf{R}_n + \mathbf{R}_m). \quad (4.8)$$

In the same way we can show that

$$U(\mathbf{R}_m)U(\mathbf{R}_n) = e^{-2\pi i \frac{p}{q} n_1 m_2} U(\mathbf{R}_n + \mathbf{R}_m). \quad (4.9)$$

From Eqs. (4.8) and (4.9), we have

$$U(\mathbf{R}_n)U(\mathbf{R}_m) = e^{-2\pi i \frac{p}{q}(m_1 n_2 - n_1 m_2)} U(\mathbf{R}_m)U(\mathbf{R}_n). \quad (4.10)$$

From this relation, if we take the set of the magnetic translation operators such as

$$\{U(\mathbf{t}_n) | \mathbf{t}_n = n_1 \mathbf{a}_1 + n_2 q \mathbf{a}_2\}, \quad (4.11)$$

then this set is shown to form an Abelian group [45]. Namely, we have

$$U(\mathbf{t}_n)U(\mathbf{t}_m) = U(\mathbf{t}_m)U(\mathbf{t}_n). \quad (4.12)$$

Note that the set of translation vector \mathbf{t}_n represents a two-dimensional rectangular lattice with a unit cell of sides a and aq (see, Fig. 4.1). In general, the eigen functions of the Hamiltonian, which belongs to a degenerate level, form basis functions of the irreducible representations (IRs) of the symmetry group of the Hamiltonian [46, 47]. In addition, all IRs of an Abelian group are necessarily one-dimensional [47]. Therefore, eigen functions $\Phi_k(\mathbf{r})$ are basis functions of IRs of the Abelian group Eq. (4.11), we have

$$U(\mathbf{t}_n)\Phi_k(\mathbf{r}) = C(\mathbf{t}_n)\Phi_k(\mathbf{r}), \quad (4.13)$$

where $C(\mathbf{t}_n)$ is the IR of the Abelian group. The normalization condition on $C(\mathbf{t}_n)\Phi_k(\mathbf{r})$ and Eq. (4.12) lead to

$$C(\mathbf{t}_n) = e^{i\mathbf{k}\cdot\mathbf{t}_n}, \quad (4.14)$$

with a wave vector \mathbf{k} that is given by

$$\mathbf{k} = k_1 \mathbf{b}_1 + k_2 \mathbf{b}_2. \quad (4.15)$$

In Eq. (4.15), k_1 and k_2 are the real numbers that satisfy $-0.5 \leq k_1, k_2 < 0.5$, and \mathbf{b}_1 and \mathbf{b}_2 are ‘‘magnetic reciprocal lattice vectors’’ defined as

$$\mathbf{b}_1 = \frac{2\pi}{a} \mathbf{e}_x; \quad \mathbf{b}_2 = \frac{2\pi}{qa} \mathbf{e}_y \quad (4.16)$$

From Eqs. (4.15) and (4.16), the ‘‘magnetic first Brillion zone’’ is denoted by a rectangle with length $2\pi/qa$ and width $2\pi/a$ (see, Fig. 4.2). Using Eqs. (4.3), (4.13) and (4.14), we have

$$\Phi_k(\mathbf{r} - \mathbf{t}_n) = e^{i\mathbf{k}\cdot\mathbf{t}_n} e^{ieBt_{nx}y/\hbar} \Phi_k(\mathbf{r}). \quad (4.17)$$

Equation (4.17) is regarded as the extension of the Bloch theorem for electron that move in a periodic potential of the crystal and uniform magnetic field. Namely, Eq. (4.17) may be referred to as the ‘Magnetic Bloch theorem’. Compared to the conventional Bloch theorem,

the phase factor $\exp(ieBt_{nx}y/\hbar)$ is additionally multiplied to the right hand side. Of course, Eq. (4.17) is reduced to the conventional Bloch theorem when $B = 0$.

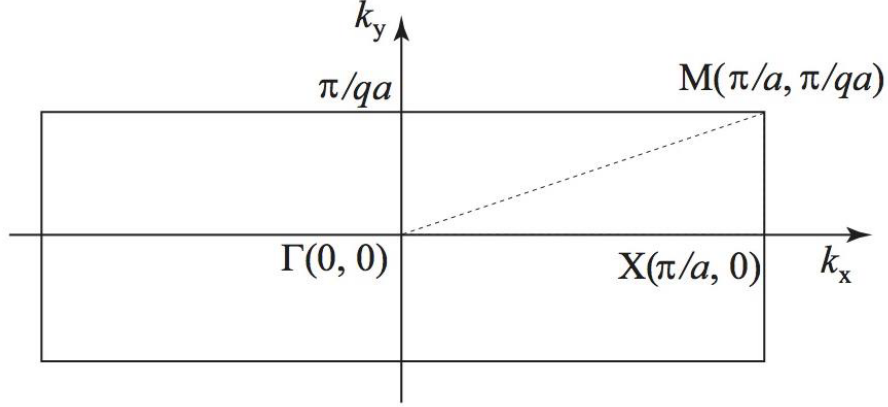


Fig. 4.2 Magnetic first Brillouin zone for a two-dimensional square lattice immersed in the uniform magnetic field [38].

4.2 Reduction of simultaneous equations via the magnetic Bloch theorem

All lattice vector \mathbf{R}_n can be expressed in terms of \mathbf{t}_n as

$$\mathbf{R}_n = \mathbf{t}_n + Iae_y, \quad (4.18)$$

where $I = 0, 1, 2, \dots, q-1$, integer. By using Eq. (4.18), Eq. (3.5) can be written as

$$\Phi_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{t}_n} \sum_{\xi} \sum_{I=0}^{q-1} C_{\mathbf{k}}^{\xi}(\mathbf{t}_n + Iae_y) \psi_{\xi}^{a_i, \mathbf{t}_n + Iae_y}(\mathbf{r}). \quad (4.19)$$

Similarly, we have

$$\Phi_{\mathbf{k}}(\mathbf{r} - \mathbf{t}_m) = \sum_{\mathbf{t}_n} \sum_{\xi} \sum_{I=0}^{q-1} C_{\mathbf{k}}^{\xi}(\mathbf{t}_n + Iae_y) \psi_{\xi}^{a_i, \mathbf{t}_n + Iae_y}(\mathbf{r} - \mathbf{t}_m). \quad (4.20)$$

Substituting Eqs. (4.19) and (4.20) into Eq. (4.17), we have

$$\sum_{\mathbf{t}_n} \sum_{\xi} \sum_{I=0}^{q-1} C_{\mathbf{k}}^{\xi}(\mathbf{t}_n + Iae_y) \psi_{\xi}^{a_i, \mathbf{t}_n + Iae_y}(\mathbf{r} - \mathbf{t}_m) = e^{-\frac{i}{\hbar} \chi(\mathbf{r}, \mathbf{t}_n)} e^{i\mathbf{k} \cdot \mathbf{t}_m} \sum_{\mathbf{t}_n} \sum_{\xi} \sum_{I=0}^{q-1} C_{\mathbf{k}}^{\xi}(\mathbf{t}_n + Iae_y) \psi_{\xi}^{a_i, \mathbf{t}_n + Iae_y}(\mathbf{r}). \quad (4.21)$$

In order to get the relationship between coefficients $C_{\mathbf{k}}^{\xi}(\mathbf{t}_\ell + Iae_y)$ by means of Eq. (4.21),

let us consider the relation between $\psi_\xi^{a_i, t_n + Iae_y}(\mathbf{r} - \mathbf{t}_m)$ and $\psi_\xi^{a_i, t_n + Iae_y}(\mathbf{r})$ that appear in Eq. (4.21). Let $\psi_\xi^{a_i, t_n + Iae_y}(\mathbf{r})$ obey the following Dirac equation

$$\left[c\alpha \cdot \{ \mathbf{P} + e\mathbf{A}(\mathbf{r}) \} + \beta mc^2 + V_{a_i}(\mathbf{r} - \mathbf{t}_n - Iae_y) \right] \psi_\xi^{a_i, t_n + Iae_y}(\mathbf{r}) = E_\xi^{t_n + Iae_y} \psi_\xi^{a_i, t_n + Iae_y}(\mathbf{r}).$$

Changing the variable from \mathbf{r}' to $\mathbf{r} + \mathbf{t}_m$, we have

$$\begin{aligned} \left[c\alpha \cdot \{ \mathbf{P}' + e\mathbf{A}(\mathbf{r}' - \mathbf{t}_m) \} + \beta mc^2 + V_{a_i}(\mathbf{r}' - \mathbf{t}_n - Iae_y - \mathbf{t}_m) \right] \psi_\xi^{a_i, t_n + Iae_y}(\mathbf{r}' - \mathbf{t}_m) \\ = E_\xi^{t_n + Iae_y} \psi_\xi^{a_i, t_n + Iae_y}(\mathbf{r}' - \mathbf{t}_m). \end{aligned}$$

According to gauge transformation, $\mathbf{A}(\mathbf{r}')$ and $\mathbf{A}(\mathbf{r}' - \mathbf{t}_m)$ are related as

$$\mathbf{A}(\mathbf{r}' - \mathbf{t}_m) = \mathbf{A}(\mathbf{r}') + \nabla \chi(\mathbf{r}', \mathbf{t}_m).$$

Using gauge transformation and changing the variable from \mathbf{r}' to \mathbf{r} and \mathbf{p}' to \mathbf{p} , we have

$$\begin{aligned} \left[c\alpha \cdot \{ \mathbf{P} + e\mathbf{A}(\mathbf{r}) + e\nabla \chi(\mathbf{r}, \mathbf{t}_m) \} + \beta mc^2 + V_{a_i}(\mathbf{r} - \mathbf{t}_n - Iae_y - \mathbf{t}_m) \right] \psi_\xi^{a_i, t_n + Iae_y}(\mathbf{r} - \mathbf{t}_m) \\ = E_\xi^{t_n + Iae_y} \psi_\xi^{a_i, t_n + Iae_y}(\mathbf{r} - \mathbf{t}_m). \end{aligned} \quad (4.22)$$

On the other hand, $\psi_\xi^{a_i, t_n + Iae_y + t_m}(\mathbf{r})$ also obey Dirac equation

$$\left[c\alpha \cdot \{ \mathbf{P} + e\mathbf{A}(\mathbf{r}) \} + \beta mc^2 + V_{a_i}(\mathbf{r} - \mathbf{t}_n - Iae_y - \mathbf{t}_m) \right] \psi_\xi^{a_i, t_n + Iae_y + t_m}(\mathbf{r}) = E_\xi^{t_n + Iae_y + t_m} \psi_\xi^{a_i, t_n + Iae_y + t_m}(\mathbf{r}). \quad (4.23)$$

Comparing Eqs. (4.22) and (4.23), $\psi_\xi^{a_i, t_n + Iae_y}(\mathbf{r} - \mathbf{t}_m)$ and $\psi_\xi^{a_i, t_n + Iae_y + t_m}(\mathbf{r})$ are related with each other by gauge transformation of wave function as

$$\psi_\xi^{a_i, t_n + Iae_y}(\mathbf{r} - \mathbf{t}_m) = e^{-\frac{e}{\hbar} \chi(\mathbf{r}, \mathbf{t}_m)} \psi_\xi^{a_i, t_n + Iae_y + t_m}(\mathbf{r}). \quad (4.24)$$

Substituting Eq. (4.24) into Eq. (4.21), we have

$$\sum_{\mathbf{t}_n} \sum_{\xi} \sum_{I=0}^{q-1} C_k^\xi(\mathbf{t}_n + Iae_y) \psi_\xi^{a_i, t_n + Iae_y + t_m}(\mathbf{r}) = e^{ik \cdot \mathbf{t}_m} \sum_{\mathbf{t}_n} \sum_{\xi} \sum_{I=0}^{q-1} C_k^\xi(\mathbf{t}_n + Iae_y) \psi_\xi^{a_i, t_n + Iae_y}(\mathbf{r}).$$

By changing the variable $\mathbf{t}_n + \mathbf{t}_m$ to \mathbf{t}_ℓ in LHS, we have

$$\sum_{\mathbf{t}_\ell} \sum_{\xi} \sum_{I=0}^{q-1} C_k^\xi(\mathbf{t}_\ell - \mathbf{t}_m + Iae_y) \psi_\xi^{a_i, t_\ell + Iae_y}(\mathbf{r}) = e^{ik \cdot \mathbf{t}_m} \sum_{\mathbf{t}_n} \sum_{\xi} \sum_{I=0}^{q-1} C_k^\xi(\mathbf{t}_n + Iae_y) \psi_\xi^{a_i, t_n + Iae_y}(\mathbf{r}).$$

Again changing the variable \mathbf{t}_ℓ to \mathbf{t}_n in LHS, we have

$$\sum_{\mathbf{t}_n} \sum_{\xi} \sum_{I=0}^{q-1} \left\{ C_k^\xi(\mathbf{t}_n - \mathbf{t}_m + I\mathbf{a}_y) - C_k^\xi(\mathbf{t}_n + I\mathbf{a}_y) e^{ik \cdot \mathbf{t}_m} \right\} \psi_\xi^{a_i, \mathbf{t}_n + I\mathbf{a}_y}(\mathbf{r}) = 0. \quad (4.25)$$

Multiplying $\psi_\xi^{a_i, \mathbf{t}_n + I\mathbf{a}_y}(\mathbf{r})$ on the both side of Eq. (4.25) and integrating, we get

$$C_k^\xi(\mathbf{t}_n - \mathbf{t}_m + I\mathbf{a}_y) = C_k^\xi(\mathbf{t}_n + I\mathbf{a}_y) e^{ik \cdot \mathbf{t}_m}.$$

Replacing $\mathbf{t}_n - \mathbf{t}_m$ by \mathbf{t}_ℓ ,

$$C_k^\xi(\mathbf{t}_\ell + I\mathbf{a}_y) = e^{ik \cdot \mathbf{t}_n - \mathbf{t}_\ell} C_k^\xi(\mathbf{t}_n + I\mathbf{a}_y).$$

If $\mathbf{t}_n = 0$, then

$$C_k^\xi(\mathbf{t}_\ell + I\mathbf{a}_y) = e^{-ik \cdot \mathbf{t}_\ell} C_k^\xi(I\mathbf{a}_y).$$

Finally by changing the variable \mathbf{t}_ℓ to \mathbf{t}_n , we get

$$\begin{aligned} C_k^\xi(\mathbf{t}_n + I\mathbf{a}_y) &= e^{-ik \cdot \mathbf{t}_n} C_k^\xi(I\mathbf{a}_y) \\ C_k^\xi(\mathbf{t}_n + I\mathbf{a}_2) &= e^{-ik \cdot \mathbf{t}_n} C_k^\xi(I\mathbf{a}_2). \end{aligned} \quad (4.26)$$

It should be noted that all lattice vectors \mathbf{R}_n are expressed as $\mathbf{t}_n + I\mathbf{a}_2 = (n_1q + I)\mathbf{a}_x + n_2\mathbf{a}_y$. Equation (4.26) means that all coefficients $C_k^\square(\mathbf{t}_n + I\mathbf{a}_2)$ can be obtained by using Eq. (4.26) if we get q coefficients $\{C_k^\xi(I\mathbf{a}_2) | I = 0, 1, 2, \dots, q-1\}$.

By replacing \mathbf{R}_m with $\mathbf{t}_m + I'\mathbf{a}_2$ ($I' = 0, 1, 2, \dots, q-1$), and using Eqs. (4.26) and (3.74), we have

$$\begin{aligned} \left\{ \bar{\varepsilon}_{n'\ell'J'} + \Delta \bar{\varepsilon}_{n'\ell'JM'} + \frac{eB}{2m} \left(\frac{2J'+1}{2\ell'+1} \right) \hbar M' \right\} C_k^{n'\ell'JM'}(I'\mathbf{a}_2) + \sum_{n\ell JM} \sum_W e^{-i\frac{eB}{2\hbar} \mathbf{T}_{Wx} \cdot \mathbf{d}_j \{ \mathbf{T}_{Wy} + 2I'\mathbf{a} \}} \\ \times \mathbf{t}_{n'\ell'J'M', in\ell JM}(\mathbf{T}_W) C_k^{n\ell JM}(\mathbf{T}_W + I'\mathbf{a}_2) = E_k C_k^{n'\ell'JM'}(I'\mathbf{a}_2). \end{aligned} \quad (4.27)$$

In deriving Eq. (4.27), we use the relation $\exp(-ieB\mathbf{T}_{Wx} \cdot \mathbf{t}_{m_y} / \hbar) = 1$, which is easily shown by considering the positions of the neighboring atoms. In this case, it should be noted that the same atoms are located on the lattice points and therefore dependencies on a_i and \mathbf{d}_i are omitted in Eq. (4.27). Since the vector $I\bar{\mathbf{a}}_2 + \mathbf{T}_W$ is generally rewritten in the form of $\mathbf{t}_{n\Box} + I\bar{\mathbf{a}}_2$, the coefficient $C_k^{n\ell JM}(I'\mathbf{a}_2 + \mathbf{T}_W)$ of the left-hand side of Eq. (4.27) can be rewritten as

$$C_k^{n\ell JM}(I\bar{\mathbf{a}}_2 + \mathbf{T}_W) = e^{i\mathbf{k} \cdot \mathbf{t}_{n\Box}} C_k^{n\ell JM}(I\bar{\mathbf{a}}_2) \quad (4.28)$$

Therefore Eq. (4.27) represents the simultaneous equations with a finite number of coefficients ($C_k^{nLM}(\mathbf{I}\mathbf{a}_2) | I = 0, 1, 2, \dots, q-1$), namely, the simultaneous equations with an infinite number of coefficients [Eq. (3.71)] are simplified to those with a finite number of coefficients owing the magnetic Bloch theorem.

4.3 Concrete expression for the simultaneous equations

We shall examine the electronic states near the Fermi level, and take into account only the relativistic hopping integral between the nearest-neighbor atoms. Since atoms have only the s -electrons ($\ell = 0$), as mentioned above, we consider the cases for $\ell = \ell' = 0$, $J = J' = 1/2$, $n = n'$, and M (or M') = $\pm 1/2$, in Eq. (4.27). The coordinates of the nearest neighbor atoms in two-dimensional square lattice are $\mathbf{T}_W = (0, a)$, $(0, -a)$, $(a, 0)$ and $(-a, 0)$, for $W = 1, 2, 3$, and 4 respectively. Let us take first nearest-neighbor atom $\mathbf{T}_1 = (0, a)$, then we have

$$\begin{aligned} \mathbf{R}_n + \mathbf{T}_1 &= \mathbf{t}_n + I' \mathbf{a}_y + \mathbf{T}_1 \\ &= \mathbf{t}_n + I' \mathbf{a}_y + \mathbf{a}_y \\ &= \mathbf{t}_n + (I' + 1) \mathbf{a}_2. \end{aligned}$$

This equation leads to

$$\begin{aligned} C_k^{n'0\frac{1}{2}M'}(\mathbf{R}_n + \mathbf{T}_1) &= C_k^{n'0\frac{1}{2}M'} \{ \mathbf{t}_n + (I' + 1) \mathbf{a}_2 \} \\ &= e^{-ik \cdot \mathbf{t}_n} C_k^{n'0\frac{1}{2}M'} \{ (I' + 1) \mathbf{a}_2 \}. \end{aligned} \quad (4.29)$$

Similarly, by taking second (\mathbf{T}_2), third (\mathbf{T}_3) and fourth (\mathbf{T}_4) nearest neighbor atoms, we have

$$\begin{aligned} C_k^{n'0\frac{1}{2}M'}(\mathbf{R}_n + \mathbf{T}_2) &= C_k^{n'0\frac{1}{2}M'} \{ \mathbf{t}_n + (I' - 1) \mathbf{a}_2 \} \\ &= e^{-ik \cdot \mathbf{t}_n} C_k^{n'0\frac{1}{2}M'} \{ (I' - 1) \mathbf{a}_2 \}, \end{aligned} \quad (4.30)$$

$$\begin{aligned} C_k^{n'0\frac{1}{2}M'}(\mathbf{R}_n + \mathbf{T}_3) &= C_k^{n'0\frac{1}{2}M'} \{ \mathbf{t}_n + \mathbf{a}_1 + I' \mathbf{a}_2 \} \\ &= e^{-ik \cdot \mathbf{t}_n} e^{-ik \cdot \mathbf{a}_x} C_k^{n'0\frac{1}{2}M'} (I' \mathbf{a}_2) \end{aligned} \quad (4.31)$$

$$\begin{aligned} C_k^{n'0\frac{1}{2}M'}(\mathbf{R}_n + \mathbf{T}_4) &= C_k^{n'0\frac{1}{2}M'} \{ \mathbf{t}_n + \mathbf{a}_1 + I' \mathbf{a}_2 \} \\ &= e^{-ik \cdot \mathbf{t}_n} e^{ik \cdot \mathbf{a}_x} C_k^{n'0\frac{1}{2}M'} (I' \mathbf{a}_2). \end{aligned} \quad (4.32)$$

Substituting Eqs. (4.29), (4.30), (4.31) and (4.32) into Eq. (4.27), we get

$$\begin{aligned}
& \left\{ \bar{\varepsilon}_{n'0\frac{1}{2}} + \Delta\bar{\varepsilon}_{n'0\frac{1}{2}M'} + \frac{eB}{m} \hbar M' \right\} C_k^{n'0\frac{1}{2}M'} (I\mathbf{a}_2) + C_k^{n'0\frac{1}{2}M'} \{(I'+1)\mathbf{a}_2\} t_{n'0\frac{1}{2}M', n'0\frac{1}{2}M'} (\mathbf{T}_1) \\
& + C_k^{n'0\frac{1}{2}M'} \{(I'-1)\mathbf{a}_2\} t_{n'0\frac{1}{2}M', n'0\frac{1}{2}M'} (\mathbf{T}_2) + e^{-ik \cdot a\mathbf{e}_x} e^{-2\pi i \frac{p}{q} I'} C_k^{n'0\frac{1}{2}M'} (I\mathbf{a}_2) t_{n'0\frac{1}{2}M', n'0\frac{1}{2}M'} (\mathbf{T}_3) \\
& + e^{ik \cdot a\mathbf{e}_x} e^{2\pi i \frac{p}{q} I'} C_k^{n'0\frac{1}{2}M'} (I\mathbf{a}_2) t_{n'0\frac{1}{2}M', n'0\frac{1}{2}M'} (\mathbf{T}_4) = E_k C_k^{n'0\frac{1}{2}M'} (I\mathbf{a}_2) \quad (4.33)
\end{aligned}$$

According to relativistic Slater-Koster table that is derived in Chapter 2 (see, Table-I), the relativistic TB parameters for nearest neighbor atoms \mathbf{T}_1 , \mathbf{T}_2 , \mathbf{T}_3 , and \mathbf{T}_4 are equally given by $K_1 \left(n'0\frac{1}{2}, n'0\frac{1}{2} \right)_{1/2}$. Therefore, Eq. (4.33) becomes

$$\begin{aligned}
& \left\{ \bar{\varepsilon}_{n'0\frac{1}{2}} + \Delta\bar{\varepsilon}_{n'0\frac{1}{2}M'} + \frac{eB}{m} \hbar M' + 2K_1 \left(n'0\frac{1}{2}, n'0\frac{1}{2} \right)_{1/2} \cos \left[2\pi \left(k_1 + \frac{p}{q} I' \right) \right] \right\} C_k^{n'0\frac{1}{2}M'} (I\mathbf{a}_2) \\
& + K_1 \left(n'0\frac{1}{2}, n'0\frac{1}{2} \right)_{1/2} \left[C_k^{n'0\frac{1}{2}M'} \{(I'+1)\mathbf{a}_2\} + C_k^{n'0\frac{1}{2}M'} \{(I'-1)\mathbf{a}_2\} \right] = E_k C_k^{n'0\frac{1}{2}M'} (I\mathbf{a}_2). \quad (4.34)
\end{aligned}$$

It should be noted that due to Eq. (4.26), $C_k^{n'0\frac{1}{2}M\Box} \{(I\Box+1)\mathbf{a}_2\}$ and $C_k^{n'0\frac{1}{2}M\Box} \{(I\Box\Box 1)\mathbf{a}_2\}$ in Eq. (4.34) are equal to

$$C_k^{n'0\frac{1}{2}M\Box} \{(I\Box+1)\mathbf{a}_2\} = \begin{cases} e^{2\Box ik_2} C_k^{n'0\frac{1}{2}M\Box} (0) & \text{for } I\Box = q\Box 1 \\ C_k^{n'0\frac{1}{2}M\Box} \{(I\Box+1)\mathbf{a}_2\} & \text{for } I\Box \neq q\Box 1 \end{cases} \quad (4.35)$$

$$C_k^{n'0\frac{1}{2}M\Box} \{(I\Box\Box 1)\mathbf{a}_2\} = \begin{cases} e^{2\Box ik_2} C_k^{n'0\frac{1}{2}M\Box} \{(I\Box\Box 1)\mathbf{a}_2\} & \text{for } I\Box = 0 \\ C_k^{n'0\frac{1}{2}M\Box} \{(I\Box\Box 1)\mathbf{a}_2\} & \text{for } I\Box \neq 0, a \end{cases} \quad (4.36)$$

respectively. It is found from Eqs. (4.35) and (4.36) that Eq. (4.34) represents the simultaneous equations for $2q$ coefficients $\{C_k^{n'0\frac{1}{2}M} (I\mathbf{a}_2) | I = 0, 1, 2, \dots, q-1, M = \pm 1/2\}$.

This means that the MFRTB method is a generalized method that includes the Hofstadter method [8]. The matrix form of above Eq. (4.34) is

$$\begin{bmatrix} S_0 & 0 & t & 0 & \dots & 0 & e^{2\pi i k_2 t} & 0 \\ 0 & S'_0 & 0 & t & 0 & \dots & 0 & e^{2\pi i k_2 t} \\ t & 0 & S_1 & 0 & t & 0 & \dots & 0 \\ 0 & t & 0 & S'_1 & 0 & t & \dots & 0 \\ \vdots & 0 & t & 0 & S_2 & 0 & \dots & \vdots \\ 0 & \vdots & \vdots & \vdots & \vdots & \ddots & \vdots & 0 \\ e^{-2\pi i k_2 t} & 0 & \dots & 0 & t & 0 & S_{q-1} & 0 \\ 0 & e^{-2\pi i k_2 t} & 0 & \dots & 0 & t & 0 & S'_{q-1} \end{bmatrix} \begin{bmatrix} C_k^{n_0 \frac{1}{2} \frac{1}{2}}(0) \\ C_k^{n_0 \frac{1}{2} \frac{1}{2}}(0) \\ C_k^{n_0 \frac{1}{2} \frac{1}{2}}(a_2) \\ C_k^{n_0 \frac{1}{2} \frac{1}{2}}(a_2) \\ \vdots \\ \vdots \\ C_k^{n_0 \frac{1}{2} \frac{1}{2}}((q-1)a_2) \\ C_k^{n_0 \frac{1}{2} \frac{1}{2}}((q-1)a_2) \end{bmatrix} = E_k \begin{bmatrix} C_k^{n_0 \frac{1}{2} \frac{1}{2}}(0) \\ C_k^{n_0 \frac{1}{2} \frac{1}{2}}(0) \\ C_k^{n_0 \frac{1}{2} \frac{1}{2}}(a_2) \\ C_k^{n_0 \frac{1}{2} \frac{1}{2}}(a_2) \\ \vdots \\ \vdots \\ C_k^{n_0 \frac{1}{2} \frac{1}{2}}((q-1)a_2) \\ C_k^{n_0 \frac{1}{2} \frac{1}{2}}((q-1)a_2) \end{bmatrix}, \quad (4.37)$$

where

$$\begin{aligned}
t &= K_1 \left(n'0 \frac{1}{2}, n'0 \frac{1}{2} \right)_{1/2} \\
S_0 &= \bar{\varepsilon}_{n'0 \frac{1}{2}} + \Delta \bar{\varepsilon}_{n'0 \frac{1}{2} \frac{1}{2}} + \frac{eB\hbar}{2m} + 2t \cos(2\pi k_1), \\
S'_0 &= \bar{\varepsilon}_{n'0 \frac{1}{2}} + \Delta \bar{\varepsilon}_{n'0 \frac{1}{2} \frac{1}{2}} - \frac{eB\hbar}{2m} + 2t \cos(2\pi k_1), \\
S_1 &= \bar{\varepsilon}_{n'0 \frac{1}{2}} + \Delta \bar{\varepsilon}_{n'0 \frac{1}{2} \frac{1}{2}} + \frac{eB\hbar}{2m} + 2t \cos \{2\pi(k_1 + p/q)\} \\
S'_1 &= \bar{\varepsilon}_{n'0 \frac{1}{2}} + \Delta \bar{\varepsilon}_{n'0 \frac{1}{2} \frac{1}{2}} - \frac{eB\hbar}{2m} + 2t \cos \{2\pi(k_1 + p/q)\} \\
&\vdots \\
S_{q-1} &= \bar{\varepsilon}_{n'0 \frac{1}{2}} + \Delta \bar{\varepsilon}_{n'0 \frac{1}{2} \frac{1}{2}} + \frac{eB\hbar}{2m} + 2t \cos \{2\pi(k_1 + \frac{p}{q}(q-1))\} \\
S'_{q-1} &= \bar{\varepsilon}_{n'0 \frac{1}{2}} + \Delta \bar{\varepsilon}_{n'0 \frac{1}{2} \frac{1}{2}} - \frac{eB\hbar}{2m} + 2t \cos \{2\pi(k_1 + \frac{p}{q}(q-1))\}
\end{aligned}$$

If we neglect the Zeeman term, then Eq. (4.29) is reduced to an equivalent form to that of Hofstadter [8].

4.4 Results and discussions

The energy eigenvalues for the two-dimensional square lattice are calculated on the basis of Eq. (4.34). Since the qualitative shape of the energy dispersion and diagram are not depend on the choice of the values $K_1 \left(n0 \frac{1}{2}, n0 \frac{1}{2} \right)_{1/2}$ and $\bar{\varepsilon}_{n_0 \frac{1}{2}} + \Delta \bar{\varepsilon}_{n_0 \frac{1}{2} M}$, they are taken from those for the crystalline silicon, which are already listed in Tables-II and III in Chapter 2. Figure

4.3(i) shows the energy dispersion E_k for the two-dimensional square lattice in the presence of the uniform magnetic field, where p and q are fixed at 40 and 401, respectively. The inset of Fig. 4.3(i) is the magnified view. The labels indicated in the horizontal axis of Fig. 4.3(i) denote the special \mathbf{k} -points in the magnetic first Brillouin zone, which is shown in Fig. 4.2. It is found from Fig. 4.3(i) that E_k depends little on \mathbf{k} , while the band dispersion for the zero magnetic field case ordinarily depends on \mathbf{k} because it is written as the cosine curve with an amplitude of $2|K_1\left(30\frac{1}{2}, 30\frac{1}{2}\right)| = 3.4782$ eV.

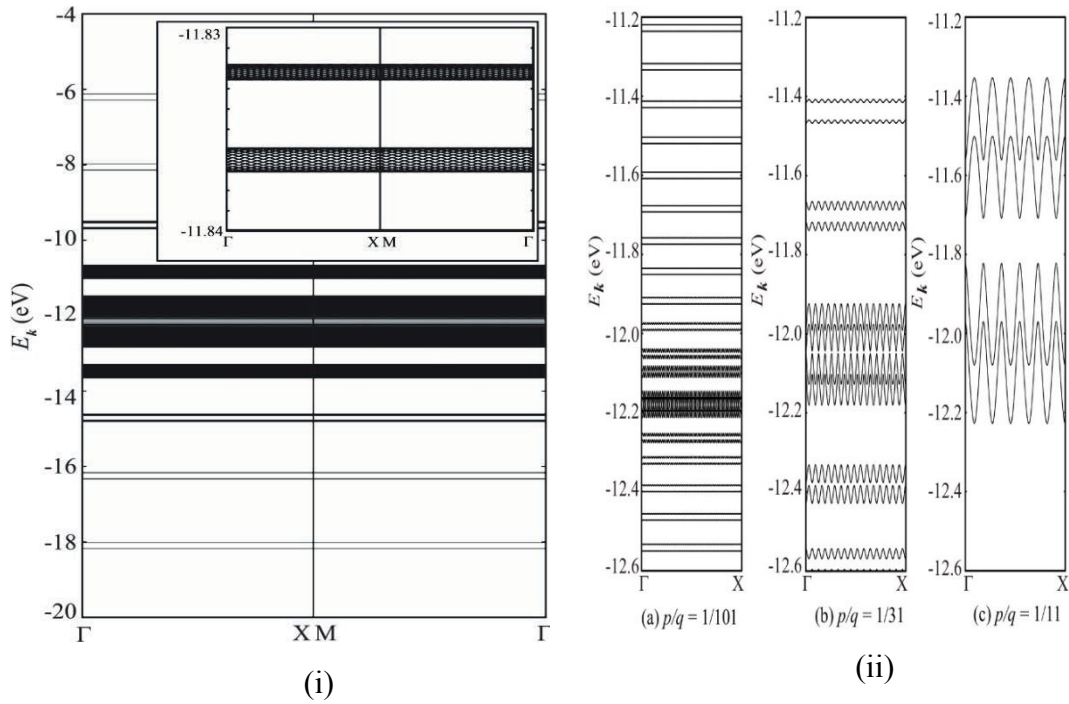


Fig. 4.3 (i) Energy dispersion for a two-dimensional square lattice immersed in a uniform magnetic field in the case of p and q are 40 and 401 respectively. The inset is the magnified view. The labels in the horizontal axis denote the Special \mathbf{k} points that are indicated in Fig. 4.2.

(ii) Magnified field dependence energy dispersion in the different cases of p/q [38].

By applying the magnetic field, the orbital motion of electrons in the plane perpendicular to the magnetic field is essentially changed corresponding to the quantization of the orbital motion of electrons in the magnetic field. As a result, E_k curve becomes nearly flat as shown in Fig. 4.3(i). The bandwidth of these flat bands is obviously dependent on the magnitude of the magnetic field. The width increases as the magnetic field becomes large, as shown in fig. 4.3(ii) ((a) - (c)). This behavior can be observed also in the crystalline silicon, which will be discussed in Chapter 5. The magnetic field dependent energy diagrams are calculated without and with Zeeman term by using Eq. (4.34). Results are shown in Figs. 4.4 (i) and 4.4 (ii) respectively, where all values of E_k for \mathbf{k} 's that correspond to the path

$\Gamma \rightarrow X \rightarrow M \rightarrow \Gamma$ of Fig. 4.2 are plotted in the each magnetic field. In these calculations, p changes from 1 to 401 with fixing q at 401. Due to the Zeeman term of Eq. (4.34), the energy diagram shown in Fig. 4.4(ii) splits into two parts. It is also confirmed that the magnitude of the band splitting becomes larger as the magnetic field increases. As can be shown in Fig. 4.4(i), Hofstadter's butterfly diagram [8] is reproduced in the case of no Zeeman term as is expected from Eq. (4.34). Namely, Fig. 4.4(i) has the properties of the butterfly diagram, which are shown by D. Hofstadter [8].

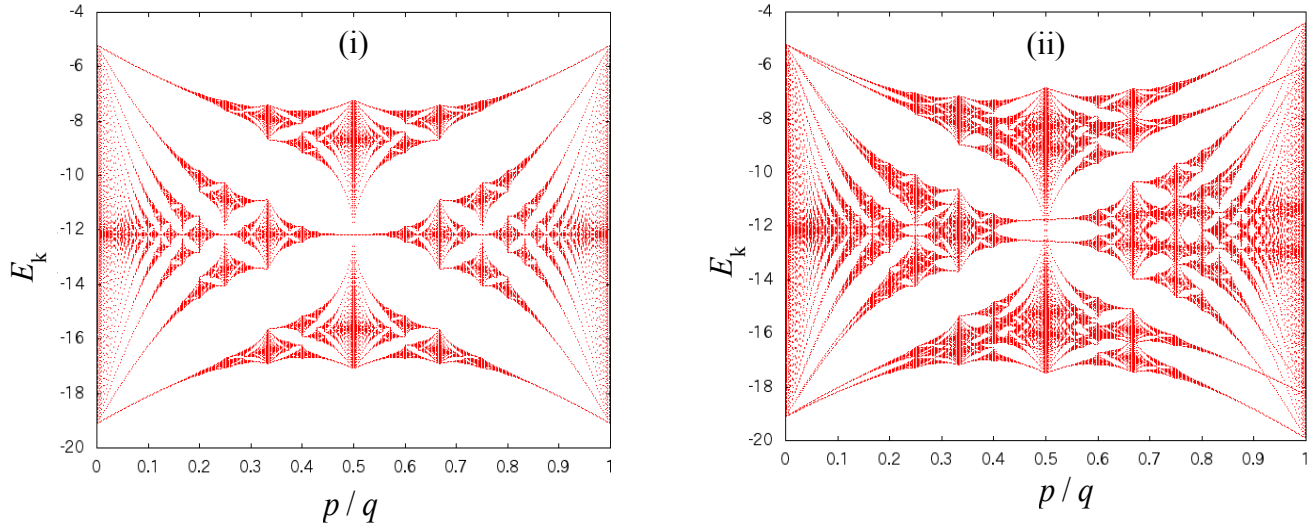


Fig. 4.4 (i) Dependence of energy diagram on the magnetic field in the absence of Zeeman term (Hofstadter's Butterfly diagram) on the basis of MFRTB method. (ii) Magnetic field dependence energy diagram with Zeeman splitting [38].

For example, the spectrum for p/q is identical with the spectra for $(p/q) + n$ (n : integer) and $-p/q$. Thus the present MFRTB method is recognized as a generalized method that includes the Hofstadter's method.

Chapter 5

Application to crystalline Silicon immersed in the uniform magnetic field

In this chapter, we shall apply the MFRTB method to a crystalline silicon immersed in the uniform magnetic field. Similar to the case of a two-dimensional square lattice (Chapter 4), nearly flat E_k curves and the magnetic field dependence of their bandwidths are observed also for this system. In addition, the present MFRTB method suggests a way to determine a formula of the magnetic field that is consistent with the magnetic Bloch theorem. With emphasis on these points, we present the electronic structure of a crystalline silicon immersed in the uniform magnetic field.

5.1 Magnetic Bloch theorem for a crystalline silicon

Crystalline silicon has the diamond structure, the lattice of which is the face centered cubic (FCC). The translation vectors of the diamond structure with the lattice constant a are given by

$$\mathbf{R}_n = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3, \quad (5.1)$$

where

$$\mathbf{a}_1 = \frac{a}{2}(\mathbf{e}_y + \mathbf{e}_z); \quad \mathbf{a}_2 = \frac{a}{2}(\mathbf{e}_x + \mathbf{e}_z); \quad \mathbf{a}_3 = \frac{a}{2}(\mathbf{e}_x + \mathbf{e}_y) \quad (5.2)$$

are the primitive translation vectors, and n_1 , n_2 and n_3 are integers. Two silicon atoms are located at $\mathbf{d}_1 = 0$ and $\mathbf{d}_2 = a(\mathbf{e}_x + \mathbf{e}_y + \mathbf{e}_z)/4$ for each lattice point, respectively. Suppose that the magnetic field is directed along z -axis having magnitude B is given by [48]

$$B = \frac{16\hbar\pi}{ea^2} \frac{p}{q}, \quad (5.3)$$

where p and q are relatively prime integers, and q is supposed to be a primitive number that is larger than 2. This form is introduced so that the solution of Eq. (3.71) is consistent with the magnetic Bloch theorem. This point will be discussed later.

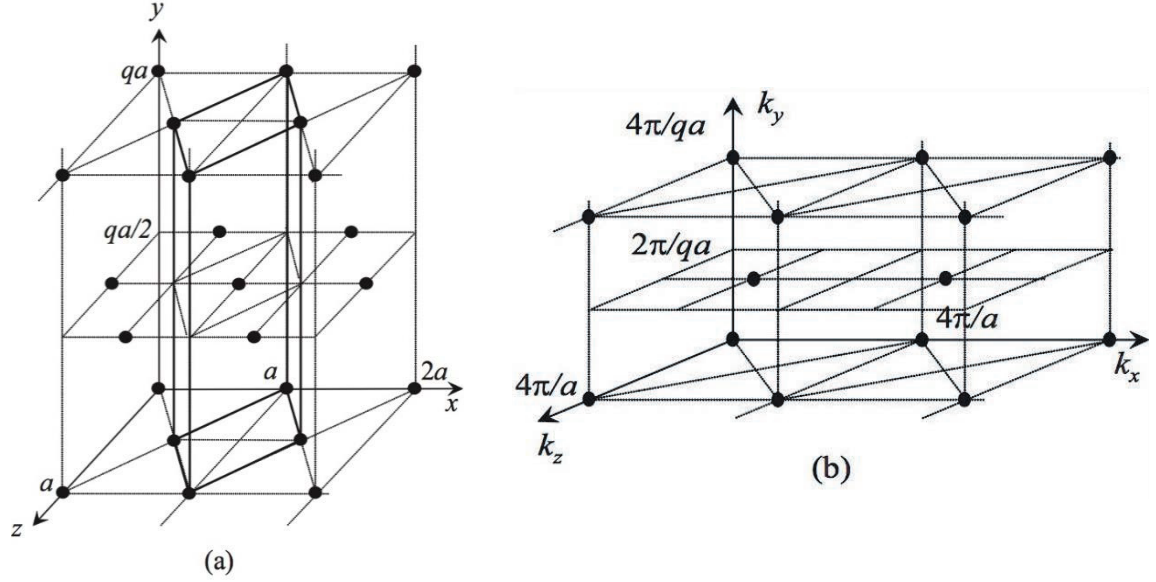


Fig. 5.1 (a) Schematic view of the lattice defined by the translation vector $\mathbf{t}_n (= n_1 q \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}'_3)$, and (b) schematic view of reciprocal lattice spanned by Eq. (5.9) [38].

Similar to the case of the two-dimensional square lattice (Chapter 4), let us consider a set of magnetic translation operators that commute with each other. By using Eqs. (4.3), (4.5), (6.1), (6.2) and (6.3), the multiplication of the two magnetic translation operators is given by

$$U(\mathbf{R}_n)U(\mathbf{R}_m) = e^{-2\pi i \frac{2p}{q}(m_1+m_2)(n_1+n_3)} U(\mathbf{R}_n + \mathbf{R}_m). \quad (5.4)$$

Reversing the order of \mathbf{R}_n and \mathbf{R}_m in the both side of Eq. (5.4), and cancelling $U(\mathbf{R}_n + \mathbf{R}_m)$ of Eq. (5.4) by using thus obtained equation, we get

$$U(\mathbf{R}_n)U(\mathbf{R}_m) = e^{-2\pi i \frac{2p}{q}(m_1+m_2)(n_1+n_3) - (m_1+m_3)(n_1+n_2)} U(\mathbf{R}_m)U(\mathbf{R}_n). \quad (5.5)$$

Using Eq. (5.5), we can easily find what set of translation operators forms the Abelian group. Specially, the following set forms the Abelian group,

$$\{U(\mathbf{t}_n) \mid \mathbf{t}_n = n_1 q \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}'_3\}, \quad (5.6)$$

where $\mathbf{a}'_3 = a(\mathbf{e}_z - \mathbf{e}_x)/2$. It is also shown that Eq. (5.6) has the smallest period of the translation among the operator sets that form an Abelian group. Note that the set of three vectors \mathbf{a}_1 , \mathbf{a}_2 and \mathbf{a}'_3 is one of the choices of the primitive translation vectors of the FCC lattice as

well as the set of \mathbf{a}_1 , \mathbf{a}_2 and \mathbf{a}_3 . The set of lattice points $\{\mathbf{t}_n\}$ forms the body centered tetragonal lattice, which is extended along the y -axis as shown in Fig. 5.1(a).

According to the general discussion on the relation between the eigen functions of the Hamiltonian and the basis functions of IRs of the symmetry group [47], we can say that the eigen function of the Hamiltonian, which are denoted by $\Phi_k(\mathbf{r})$, can be the basis functions of IRs of Eq. (5.6). In the similar way to the case of two-dimensional square lattice (Chapter 4), we have

$$U(\mathbf{t}_n)\Phi_k(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{t}_n}\Phi_k(\mathbf{r}), \quad (5.7)$$

with the wave vector \mathbf{k} that is given by

$$\mathbf{k} = k_1\mathbf{b}_1 + k_2\mathbf{b}_2 + k_3\mathbf{b}_3, \quad (5.8)$$

where k_1, k_2 and k_3 are the real numbers that varies $-0.5 \leq k_1, k_2, k_3 < 0.5$, and $\mathbf{b}_1, \mathbf{b}_2$ and \mathbf{b}_3 are ‘‘magnetic reciprocal lattice vectors’’ for the crystalline silicon, which are defined as

$$\mathbf{b}_1 = \frac{4\pi}{aq} \mathbf{e}_y; \quad \mathbf{b}_2 = \frac{2\pi}{a} (\mathbf{e}_x - \mathbf{e}_y + \mathbf{e}_z); \quad \mathbf{b}_3 = \frac{2\pi}{a} (-\mathbf{e}_x + \mathbf{e}_y + \mathbf{e}_z). \quad (5.9)$$

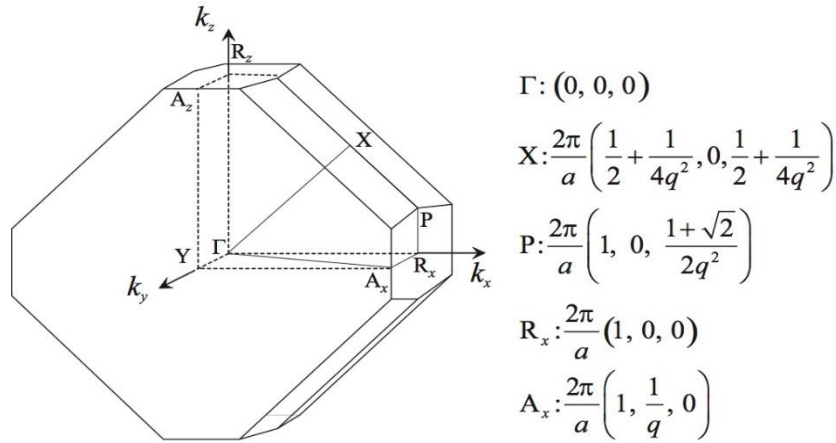


Fig. 5.2 Schematic view of the magnetic first Brillouin zone for the crystalline silicon immersed in the uniform magnetic field [38].

The reciprocal lattice spanned by Eq. (5.9) and corresponding first magnetic Brillouin zone are given in Fig. 5.1(b) and Fig. 5.2, respectively.

Equations (4.3), (4.5), and (5.7) lead to the magnetic Bloch theorem for the crystalline silicon:

$$\Phi_k(\mathbf{r} - \mathbf{t}_n) = e^{i\mathbf{k}\cdot\mathbf{t}_n} e^{ieBt_{nx}y/\hbar} \Phi_k(\mathbf{r}). \quad (5.10)$$

This theorem is used in the next section to reduce the order of the simultaneous Eq. (3.71).

5.2 Reduction of simultaneous equations via the Magnetic Bloch theorem

The lattice vectors \mathbf{R}_n is expressed by

$$\begin{aligned}\mathbf{R}_n &= \mathbf{t}_n + I\mathbf{a}_1 \\ &= (n_1q + I)\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3,\end{aligned}\quad (5.11)$$

where $I = 0, 1, 2, \dots, q-1$. Similar to the case of two-dimensional square lattice, substituting Eq. (3.5) into Eq. (5.10), and using Eqs. (3.27) and (5.11), we have

$$\sum_{\mathbf{t}_n} \sum_{\xi} \sum_{I=0}^{q-1} \sum_i \{C_k^\xi(\mathbf{t}_n + I\mathbf{a}_1 + \mathbf{d}_i - \mathbf{t}_m) - e^{ik \cdot \mathbf{t}_m} C_k^\xi(\mathbf{t}_n + I\mathbf{a}_1 + \mathbf{d}_i)\} \psi_\xi^{a_i, \mathbf{t}_n + I\mathbf{a}_1 + \mathbf{d}_i}(\mathbf{r}) = 0. \quad (5.12)$$

Utilizing the orthonormality of the basis functions, a relation between the expansion coefficients is obtained as

$$C_k^\xi(\mathbf{t}_m + I\mathbf{a}_1 + \mathbf{d}_i) = e^{-ik \cdot \mathbf{t}_m} C_k^\xi(I\mathbf{a}_1 + \mathbf{d}_i). \quad (5.13)$$

Equation (5.13) is an alternative expression of the magnetic Bloch theorem. Rewriting Eq. (3.71) by using $\mathbf{t}_m + I'\mathbf{a}_1$ instead of \mathbf{R}_m , and substituting Eq. (5.13) into this, we have

$$\begin{aligned}& \left\{ \bar{\varepsilon}_{n'\ell'J'}^{-a_j} + \Delta \varepsilon_{n'\ell'JM'}^{-a_j, \mathbf{d}_j} + \frac{eB}{2m} \left(\frac{2J'+1}{2\ell'+1} \right) \hbar M' \right\} C_k^{n'\ell'JM'}(I'\mathbf{a}_1 + \mathbf{d}_j) + \sum_{n\ell JM} \sum_W e^{-i\frac{eB}{2\hbar} \mathbf{T}_{Wx}(\mathbf{d}_j) \{ \mathbf{T}_{Wy}(\mathbf{d}_j) + 2\mathbf{t}_{my} + 2I'\mathbf{a}_{1y} + 2\mathbf{d}_{jy} \}} \\ & \times t_{n'\ell'JM', n\ell JM}(\mathbf{T}_W(\mathbf{d}_j)) C_k^{n\ell JM}(\mathbf{T}_W(\mathbf{d}_j) + I'\mathbf{a}_1 + \mathbf{d}_j) = E_k C_k^{n'\ell'JM'}(I'\mathbf{a}_1 + \mathbf{d}_j),\end{aligned}\quad (5.14)$$

where we remove the superscripts of the hopping integral since all sites are, of course, occupied by the silicon atoms. It should be noticed that since $\mathbf{T}_W(\mathbf{d}_j) + I'\mathbf{a}_1 + \mathbf{d}_j$ denotes the position of Si atom, this vector is rewritten in the form of $\mathbf{t}_n + I''\mathbf{a}_1 + \mathbf{d}_i$. Therefore $C_k^{n\ell JM}(\mathbf{T}_W(\mathbf{d}_j) + I'\mathbf{a}_1 + \mathbf{d}_j)$ in the left hand side of Eq. (5.14) is rewritten as

$$C_k^{n\ell JM}(\mathbf{T}_W(\mathbf{d}_j) + I'\mathbf{a}_1 + \mathbf{d}_j) = e^{-ik \cdot \mathbf{t}_n} C_k^{n\ell JM}(I''\mathbf{a}_1 + \mathbf{d}_i), \quad (5.15)$$

where Eq. (5.13) is used. Equations (5.14) and (5.15) mean the reduction of the simultaneous equation (3.71). That is to say, they are regarded as the simultaneous equations for the finite number of coefficients $\{C_k^{n\ell JM}(I\mathbf{a}_1 + \mathbf{d}_i) \mid I = 0, 1, 2, \dots, q-1; \quad i = 1, 2; \quad n\ell JM\}$.

Equation (5.14) includes an important suggestion for a way to determine the formula of the magnetic field. Here, we shall give an important comment on the formula of the magnetic field that is consistent with magnetic Bloch theorem. If the magnetic field were given by

$$B = 8\pi\hbar / ea^2(p/q) \quad (5.16)$$

instead of Eq. (5.3), then the phase factor $\exp(-ieBT_{W_x}(\mathbf{d}_j)t_{my}/\hbar)$ that appears in Eq. (5.14) would not be equal to 1 and would depend on t_{my} . In this case, the simultaneous equations for the set of coefficients $\{C_k^{n\ell JM}(\mathbf{I}\mathbf{a}_1 + \mathbf{d}_i) | I = 0, 1, 2, \dots, q-1; i = 1, 2, \dots, n\ell JM\}$ vary with t_{my} although the set of coefficients, of course intrinsically, does not depend on t_{my} . This means that the original simultaneous equations [Eq. (3.71)] for the magnetic field Eq. (5.16) lead to solutions that are not consistent with the magnetic Bloch theorem [Eq. (5.13)]. This difficulty seems to come from the incompleteness of the set of basis functions $\psi_{\mathbf{R}_n + \mathbf{d}_i}^{\xi, a_i}(\mathbf{r})$. In order to avoid this difficulty, the magnitude of magnetic field is chosen in the form of Eq. (5.3) [49]. Namely, if the form of the magnetic field is chosen like Eq. (5.3), then the phase factor $\exp(-ieBT_{W_x}(\mathbf{d}_j)t_{my}/\hbar)$ is shown to be equal to 1, which makes the solution of Eq. (5.14) consistent with the magnetic Bloch theorem. Considering this fact, i.e., $\exp(-ieBT_{W_x}(\mathbf{d}_j)t_{my}/\hbar) = 1$, Eq. (6.14) is finally rewritten as

$$\left\{ \bar{\varepsilon}_{n\ell'J'}^{-a_j} + \Delta \varepsilon_{n\ell'JM'}^{-a_j, d_j} + \frac{eB}{2m} \left(\frac{2J'+1}{2\ell'+1} \right) \hbar M' \right\} C_k^{n\ell'JM'}(\mathbf{I}\mathbf{a}_1 + \mathbf{d}_j) + \sum_{n\ell JM} \sum_W e^{-i\frac{eB}{2\hbar} T_{W_x}(\mathbf{d}_j) \{T_{W_y}(\mathbf{d}_j) + 2I'a_{1y} + 2d_{1y}\}} \times t_{n\ell'JM', n\ell JM}(\mathbf{T}_W(\mathbf{d}_j)) C_k^{n\ell JM}(\mathbf{T}_W(\mathbf{d}_j) + \mathbf{I}\mathbf{a}_1 + \mathbf{d}_j) = E_k C_k^{n\ell'JM'}(\mathbf{I}\mathbf{a}_1 + \mathbf{d}_j). \quad (5.17)$$

Table-IV. Phase factors $\exp[-ieBT_{W_x}(\mathbf{d}_1) \{T_{W_y}(\mathbf{d}_1) + 2I'a_{1y} + 2d_{1y}\} / 2\hbar]$ and the coefficients $C_k^{n\ell JM}(\mathbf{T}_W(\mathbf{d}_1) + \mathbf{I}\mathbf{a}_1 + \mathbf{d}_1)$ that appear on the LHS of Eq. (5.17).

W	$\mathbf{T}_W(\mathbf{d}_1)$	$e^{-i\frac{eB}{2\hbar} T_{W_x}(\mathbf{d}_1) \{T_{W_y}(\mathbf{d}_1) + 2I'a_{1y} + 2d_{1y}\}}$	$C_k^{n\ell JM}(\mathbf{T}_W(\mathbf{d}_1) + \mathbf{I}\mathbf{a}_1 + \mathbf{d}_1)$
1	$\frac{a}{4}(1, 1, 1)$	$e^{-2\pi i \frac{p}{q} (I' + \frac{1}{4})}$	$C_k^{n\ell JM}(\mathbf{I}\mathbf{a}_1 + \mathbf{d}_2)$
2	$\frac{a}{4}(1, -1, -1)$	$e^{-2\pi i \frac{p}{q} (I' - \frac{1}{4})}$	$e^{2\pi i k_3} C_k^{n\ell JM}((I' - 1)\mathbf{a}_1 + \mathbf{d}_2)$
3	$\frac{a}{4}(-1, 1, -1)$	$e^{2\pi i \frac{p}{q} (I' + \frac{1}{4})}$	$e^{2\pi i k_2} C_k^{n\ell JM}(\mathbf{I}\mathbf{a}_1 + \mathbf{d}_2)$
4	$\frac{a}{4}(-1, -1, 1)$	$e^{2\pi i \frac{p}{q} (I' - \frac{1}{4})}$	$C_k^{n\ell JM}((I' - 1)\mathbf{a}_1 + \mathbf{d}_2)$

5.3 Concrete expressions for the simultaneous equations

Let us give the concrete expressions for the simultaneous equations used in the actual calculations. In order to consider the electronic states in the vicinity of the Fermi level, we shall take s and p electrons of the outer shells of the Si atom in calculating the hopping integrals. Namely, we consider the hopping integrals between the following eight shells:

$$(n, \ell, J, M) = \left(3, 0, \frac{1}{2}, \pm \frac{1}{2}\right), \left(3, 1, \frac{1}{2}, \pm \frac{1}{2}\right), \left(3, 1, \frac{3}{2}, \pm \frac{1}{2}\right), \left(3, 1, \frac{3}{2}, \pm \frac{3}{2}\right). \quad (5.18)$$

Furthermore, we consider only the electron hopping between the nearest neighbor atoms. Specifically four kinds of vectors $\mathbf{T}_W(\mathbf{d}_j)$ ($W = 1$ to 4) are considered in the calculations.

Table-V. Phase factors $\exp[-ieBT_{Wx}(\mathbf{d}_2)\{T_{Wy}(\mathbf{d}_2) + 2I'a_{1y} + 2d_{2y}\}/2\hbar]$ and the coefficients $C_k^{n\ell JM}(\mathbf{T}_W(\mathbf{d}_2) + I'\mathbf{a}_1 + \mathbf{d}_2)$ that appear on the LHS of Eq. (5.17).

W	$\mathbf{T}_W(\mathbf{d}_2)$	$e^{-i\frac{eB}{2\hbar}T_{Wx}(\mathbf{d}_2)(T_{Wy}(\mathbf{d}_2) + 2I'a_{1y} + 2d_{2y})}$	$C_k^{n\ell JM}(\mathbf{T}_W(\mathbf{d}_2) + I'\mathbf{a}_1 + \mathbf{d}_2)$
1	$\frac{a}{4}(1, 1, 1)$	$e^{\frac{2\pi i P}{q}(I' + \frac{1}{2})}$	$C_k^{n\ell JM}(I'\mathbf{a}_1)$
2	$\frac{a}{4}(1, -1, -1)$	$e^{\frac{2\pi i P}{q}(I' + \frac{3}{4})}$	$e^{-2\pi i k_3} C_k^{n\ell JM}((I' + 1)\mathbf{a}_1)$
3	$\frac{a}{4}(-1, 1, -1)$	$e^{-\frac{2\pi i P}{q}(I' + \frac{1}{2})}$	$e^{-2\pi i k_2} C_k^{n\ell JM}(I'\mathbf{a}_1)$
4	$\frac{a}{4}(-1, -1, 1)$	$e^{-\frac{2\pi i P}{q}(I' + \frac{3}{4})}$	$C_k^{n\ell JM}((I' + 1)\mathbf{a}_1)$

In the following, we show the concrete expression for Eq. (5.17) in the case for (i) $\mathbf{d}_j = \mathbf{d}_1$ and (ii) $\mathbf{d}_j = \mathbf{d}_2$, individually. The phase factors $\exp[-ieBT_{Wx}(\mathbf{d}_j)\{T_{Wy}(\mathbf{d}_j) + 2I'a_{1y} + 2d_{jy}\}/2\hbar]$ and the coefficients $C_k^{n\ell JM}(\mathbf{T}_W(\mathbf{d}_j) + I'\mathbf{a}_1 + \mathbf{d}_j)$ in the left hand side of Eq. (5.17) are given in Tables IV and V for both cases [(i) and (ii)]. Using these, we have

(i) For $\mathbf{d}_j = \mathbf{d}_1$,

$$\begin{aligned} & \left\{ \bar{\varepsilon}_{3\ell J'}^{Si} + \Delta \varepsilon_{3\ell JM'}^{-Si, \mathbf{d}_1} + \frac{eB}{2m} \left(\frac{2J' + 1}{2\ell' + 1} \right) \hbar M' \right\} C_k^{3\ell JM'}(I'\mathbf{a}_1) + \sum_{\ell JM} \left[e^{-\frac{2\pi i P}{q}(I' + \frac{1}{4})} t_{3\ell JM', 3\ell JM}(\mathbf{T}_1(\mathbf{d}_1)) \right. \\ & + e^{\frac{2\pi i P}{q}(I' + \frac{1}{4})} e^{2\pi i k_2} t_{3\ell JM', 3\ell JM}(\mathbf{T}_3(\mathbf{d}_1)) \left. \right] C_k^{3\ell JM}(I'\mathbf{a}_1 + \mathbf{d}_2) + \sum_{\ell JM} \left[e^{-\frac{2\pi i P}{q}(I' - \frac{1}{4})} e^{2\pi i k_3} t_{3\ell JM', 3\ell JM}(\mathbf{T}_2(\mathbf{d}_1)) \right. \\ & + e^{\frac{2\pi i P}{q}(I' - \frac{1}{4})} t_{3\ell JM', 3\ell JM}(\mathbf{T}_4(\mathbf{d}_1)) \left. \right] C_k^{3\ell JM}((I' - 1)\mathbf{a}_1 + \mathbf{d}_2) = E_k C_k^{3\ell JM'}(I'\mathbf{a}_1) \end{aligned} \quad (5.19)$$

with

$$C_k^{3\ell JM}((I' - 1)\mathbf{a}_1 + \mathbf{d}_2) = \begin{cases} e^{2\pi i k_1} C_k^{3\ell JM}((q - 1)\mathbf{a}_1 + \mathbf{d}_2) & \text{for } I' = 0, \\ C_k^{3\ell JM}((I' - 1)\mathbf{a}_1 + \mathbf{d}_2) & \text{for } I' \neq 0. \end{cases} \quad (5.20)$$

(ii) For $\mathbf{d}_j = \mathbf{d}_2$,

$$\begin{aligned}
& \left\{ \bar{\varepsilon}_{3\ell'J'}^{Si} + \Delta \varepsilon_{3\ell'JM'}^{-Si, \mathbf{d}_2} + \frac{eB}{2m} \left(\frac{2J'+1}{2\ell'+1} \right) \hbar M' \right\} C_k^{3\ell'JM'}(I'\mathbf{a}_1 + \mathbf{d}_2) + \sum_{\ell JM} \left[e^{\frac{2\pi i p}{q} (I'+\frac{1}{2})} t_{3\ell'JM', 3\ell JM}(\mathbf{T}_1(\mathbf{d}_2)) \right. \\
& + e^{-\frac{2\pi i p}{q} (I'+\frac{1}{2})} e^{-2\pi i k_2} t_{3\ell'JM', 3\ell JM}(\mathbf{T}_3(\mathbf{d}_2))] C_k^{3\ell JM}(I'\mathbf{a}_1) + \sum_{\ell JM} \left[e^{\frac{2\pi i p}{q} (I'+\frac{3}{4})} e^{-2\pi i k_3} t_{3\ell'JM', 3\ell JM}(\mathbf{T}_2(\mathbf{d}_2)) \right. \\
& \left. + e^{-\frac{2\pi i p}{q} (I'+\frac{3}{4})} t_{3\ell'JM', 3\ell JM}(\mathbf{T}_4(\mathbf{d}_2)) \right] C_k^{3\ell JM}((I'+1)\mathbf{a}_1) = E_k C_k^{3\ell'JM'}(I'\mathbf{a}_1 + \mathbf{d}_2) \quad (5.21)
\end{aligned}$$

with

$$C_k^{3\ell JM}((I'+1)\mathbf{a}_1) = \begin{cases} e^{-2\pi i k_1} C_k^{3\ell JM}(0) & \text{for } I' = q-1, \\ C_k^{3\ell JM}((I'+1)\mathbf{a}_1) & \text{for } I' \neq q-1. \end{cases} \quad (6.22)$$

In Eqs. (5.19) and (5.21), the summation on ℓ , J and M is over eight states given in Eq. (5.18). The hopping integrals can be transcribed by the TB parameters with the aid of the relativistic Slater-Koster table shown in Table I. Equations (5.19) and (5.21) form simultaneous equations with a finite number of coefficients $\{C_k^{3\ell JM}(I\mathbf{a}_1 + \mathbf{d}_j) | I = 0, 1, 2, \dots, q-1; (3, \ell, J, M) = \text{Eq.}(5.18)\}$.

5.4 Energy bands for a crystalline silicon immersed in the uniform magnetic field

5.4.1 Energy dispersion

Figure 5.3(i) shows the energy bands for crystalline silicon immersed in the uniform magnetic field, where p and q are fixed at 1 and 101, respectively. We have $16q$ ($=1616$) energy bands in the energy dispersion because $16q$ eigenvalues of E_k are obtained for each \mathbf{k} . The labels indicated in the horizontal axis of Fig. 5.3(i) denote the points in the magnetic first Brillouin zone [Fig. 5.2]. Points p , R_x and A_x are quite close to each other owing to the present magnetic field. Their coordinates are explicitly given in Fig. 5.2. It is found from Fig. 5.3(i) that values of E_k obviously change depending on k_z ($\Gamma - X - P - R_x$ line). This corresponds to the fact that the electron is not subjected to the Lorentz force in the z -direction, and makes the relatively large hopping along the z -direction. On the other hand, E_k depends little on k_x and k_y , and gap structures are observed in the $R_x - A_x - \Gamma$ line, similar to the case of two-dimensional square lattice. Zooming in these flat bands for the several cases [Fig. 5.3(ii) {(a) - (e)}], we can find following five properties in the E_k curves.

(a) It is found that E_k is periodic in the $k_x - k_y$ plane. Similar to the case of two-dimensional square lattice [50], this periodicity comes from the symmetry of the crystalline silicon immersed in the z -directed magnetic field. Namely, since E_k is a periodic function of k_y ,

with the period of $4\pi/aq$ that corresponds to the width of the first magnetic Brillouin zone, E_k also becomes a periodic function of k_x with the same period.

(b) In order to investigate the gap structures observed in the $k_x - k_y$ plane, let us consider the case where the rational number p/q in Eq. (5.3) is given by $1/q$ ($p=1$). It is expected that the number of allowed bands is approximately proportional to q , because the number of energy bands E_k is given by $16q$. Indeed, we find the relation such that $N \propto 6q$, where N is the number of allowed bands, which is directly confirmed through numerical calculations. From this property, the band width is expected to decrease with q . The magnetic field dependence of the band width will be discussed in the property (d).

(c) Next, we consider the case where p/q is nearly equal to $1/q'$, i.e., $q \approx pq'$, where q' is a prime integer. Figures 5.3(ii) {(a) – (e)} show the energy bands in the $k_x - k_y$ plane for the cases of $1/q' = 1/11$, $p/q = 2/23$, $3/31$, $4/41$, and $5/53$, respectively. It is also found from these figures that p allowed bands are observed in the case of p/q , while one allowed band is observed in the case of $1/q'$. Therefore N allowed bands for the case of $1/q'$ are respectively divided into p allowed bands for the case of p/q .

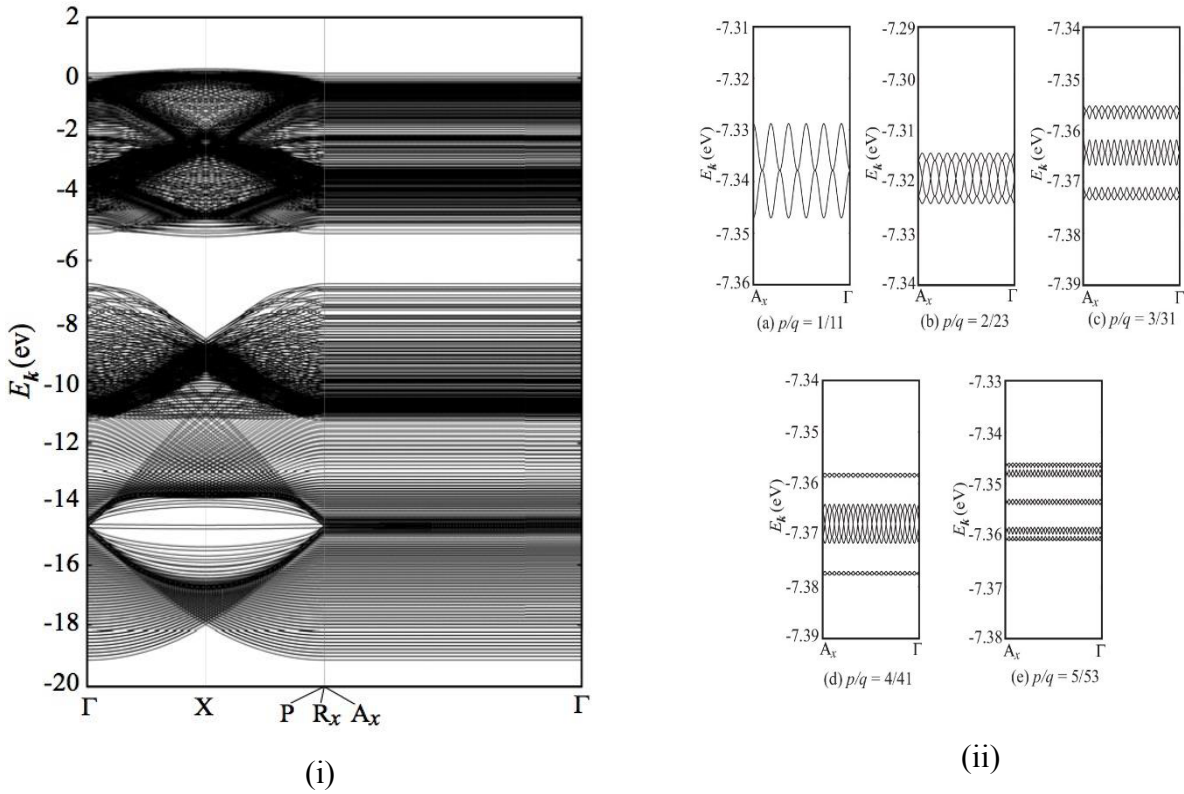


Fig. 5.3 (i) Energy dispersion for a crystalline silicon immersed in the uniform magnetic field. The value of p and q are 1 and 101 respectively. The labels in the horizontal axis are denoted by special k points that are indicated in Fig. 5.2. (ii) Magnified view of energy dispersion (flat band) in the $k_x - k_y$ plane for different cases of p/q [38].

This property is recognized as follows. Because of the relation $q \approx pq'$, in the case of p/q , the period of t_n along the \mathbf{a}_1 direction is p times longer than that in the case of $1/q'$. Therefore, due to the folding of the magnetic first Brillouin zone, p energy gaps may be induced at the boundaries of the magnetic first Brillouin zone by the Bragg reflection. This is the reason why the number of allowed bands in the case of p/q is p times more than that in the case of $1/q'$ ($\approx p/q$).

(d) In the case of p/q , the energy width of the cluster consisting of p allowed bands is referred to as the cluster width. It is found from Figs. 5.3(ii) {(a) – (e)} that the energy width of the allowed band for case of $1/q'$ is nearly equal to the cluster width for the case of p/q . (Note that, although the cluster width in Fig. 5.3(ii) (b) is exceptionally a little smaller than those of the other cases [Figs. 5.3(ii) {(a) – (e)}], this discrepancy is not essential. This discrepancy comes from the error of the premise $1/q' (\approx p/q)$, i.e., the accuracy of the premise is not good in the case of $p/q = 2/23$ as compared with other cases.)

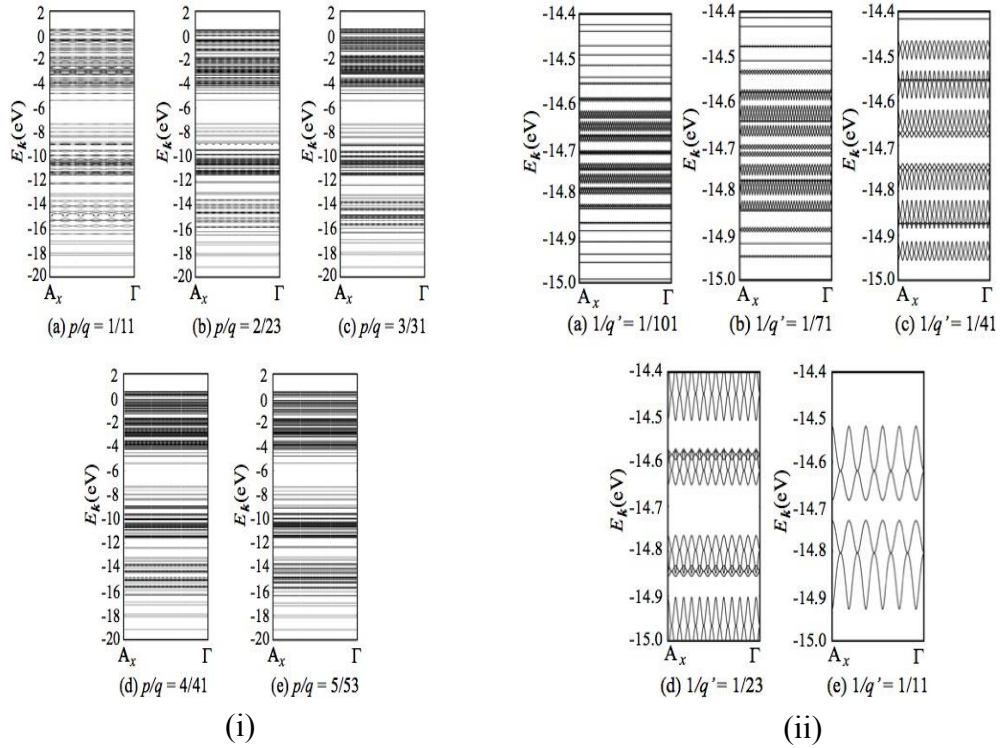


Fig. 5.4 (i) Whole energy dispersion in the $k_x - k_y$ plane for different cases of p/q . (ii) Magnetic field energy dispersion for a crystalline silicon immersed in the uniform magnetic field in the $k_x - k_y$ plane for different cases of p/q [38].

Due to this property, we can say that the outlines of the gap structures for five cases with $1/q' (\approx p/q)$ resemble each other if the full energy bands are plotted in the larger energy scale [Figs. 5.4(i) {(a) – 5.4(e)}]. Therefore we may regard the cluster width for the case of p/q as the bandwidth that is nearly identical with the real bandwidth for the case of $1/q'$.

(e) As mentioned in the property (d), the gap structure for the case of $1/q'$ is similar to those for the cases of p/q ($\approx 1/q'$). So, we shall discuss the magnetic field dependence of the bandwidth by using the bandwidth for the case of $1/q'$. Figs. 5.4(ii){(a) – (e)} show the energy bands in the $k_x - k_y$ plane for the cases of moderately weak magnetic field $p/q < 0.1$. It is found from these figures that there exist bandwidths that depend on the magnitude of the magnetic field. The bandwidth definitely increases as the magnetic field becomes large. When the magnetic field is quite weak, then the electronic states are comparably less affected by the magnetic field. At that time, the effective mass approximation seems to be valid, so that the property of the Landau level still survives in the electronic states. On the other hands, when the magnetic field increases, the electron hopping between the electronic states becomes larger, which results in making the bandwidth of the energy dispersion large.

This is easily comprehended from the following discussion. In the solids with no magnetic field, the electron hopping between the atomic orbitals generally takes some nonzero value, and correspondingly yields the nonzero width of the energy dispersion. As the magnetic field increases, the spatial broadening of the electronic state gets close to that of the usual atomic orbitals, which may facilitate the electron hopping between the two neighboring states. Therefore we can also say that the magnitude of the bandwidth corresponds to the degree of the infeasibility of the effective mass approximation in the region of moderately weak magnetic field $p/q < 0.1$.

5.4.2 Butterfly diagram for a crystalline silicon immersed in the uniform magnetic field

The magnetic field dependent energy diagrams are shown in Figs. 5.5(a) and 5.5(b). These are calculated under two conditions: One is that all values of E_k for \mathbf{k} 's that correspond to the horizontal axis of Fig. 5.3(i) are plotted in each magnetic field [Fig. 5.5(a)]. Another is that all values of E_k for \mathbf{k} 's that are in the $k_x - k_y$ plane are plotted in each magnetic field [Fig. 5.5(b)]. Due to the Zeeman term, the energy diagrams of both figures become wide as the magnetic field increases. Correspondingly, the energy diagrams for the crystalline silicon are not symmetric, similar to the case of two-dimensional square lattice [Fig. 4.4(i)]. Comparing Fig. 5.5(a) with Fig. 5.5(b), the characteristic gap structures can be found in Fig. 5.5(b), while almost all of them disappear in Fig. 5.5(a). Especially, in Fig. 5.5(b), energy diagrams that are similar to the Hofstadter's butterfly diagrams can be observed. In addition, recursive structures can be confirmed in Fig. 5.5(c). Since q are prime numbers, and since a quite small range of p/q is magnified in Fig. 5.5(c), the nonuniformity of plotted p/q , which inevitably emerges, is a little noticeable. However, we can definitely confirm the recursive patterns of the energy gaps in Fig. 5.5(c).

It is easily understood that the disappearance of gap structures in Fig. 5.5(a) is due to the fact that values of E_k strongly depend on k_z . However, the appearance of the butterfly diagrams in Figs. 5.5(b) and 5.5(c) would indicate the peculiar properties of the electronic states of crystalline silicon immersed in the magnetic field. The magnetic field dependence of gap structures of E_k bands in the $k_x - k_y$ plane is essential for the appearance of the butterfly diagrams. This means that the electronic states of the crystalline silicon immersed in

the uniform magnetic field partially loose the two-dimensional degree of freedom depending on the magnitude of the magnetic field, though the crystalline silicon itself has three-dimensional structure. That is to say, the motion of electrons in the two-dimensional plane is restricted to a degree depending on the magnitude of magnetic field, so that the energy diagram of the butterfly shape correspondingly emerges.

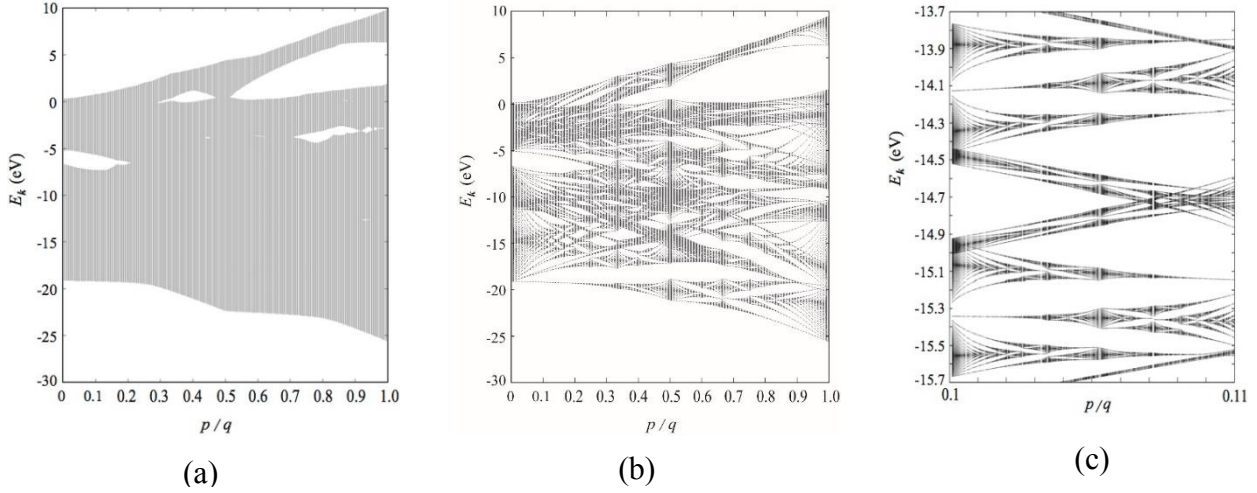


Fig. 5.5 Dependence of energy diagram on the magnetic field for a crystalline silicon (a) in the case of varying wave vectors in the magnetic first Brillouin zone (b) in the case of varying wave vectors in the $k_x - k_y$ plane of the magnetic first Brillouin zone. The magnified view of the energy diagram is shown in (c), where the recursive structure can be found [38].

Thus, it is shown by means of the MFRTB method that the butterfly diagram, which includes the recursive structures, appears in the energy diagrams of the crystalline silicon immersed in the uniform magnetic field. There is a future possibility that such energy structures are observed experimentally also in a silicon based system as already observed in the GaAs/AlGaAs heterostructure system [51,52].

5.4.3 Valance and conduction bands

As can be seen in Figs. 5.5(a), 5.5(b), and 5.3(i), when the magnetic field is weak, an energy gap appears in the vicinity of -6 eV. We shall focus on this energy gap, and show that it just corresponds to the energy gap between the valance and conduction bands. Although there exist $8q$ energy bands below and above this energy gaps, respectively, in Fig. 5.3(i), we will show that they correspond to the valance and conduction bands, respectively.

First, let us confirm the following two points. (i) As shown in Chapter 2 and Chapter 5 of section 5.2, the magnetic Bloch theorem makes the diagonalization problem of deriving all the eigenvalues of each \mathbf{k} belonging to the magnetic first Brillouin zone. This statement is straightforwardly expressed by Eqs. (4.22) and (5.15). (ii) All electronic states of the system can be indicated by the wave numbers \mathbf{k} that lie within the magnetic first Brillouin

zone. This can be easily shown by using the magnetic Bloch theorem in a similar way to the case of no magnetic field [53]. Using these two points, it is proved that the number of k involved in the magnetic first Brillouin zone is equal to that of t_n , which are distributed in the whole system. Thus, we get the following theorem: **“The total number of k -points contained in the magnetic first Brillouin zone coincides with that of the magnetic primitive unit cell in the system”**.

Next, we consider the number of electrons in the whole system. One lattice point has the two silicon atoms and correspondingly eight electrons (two set of four outer-shell electrons) belong to it. As shown in Fig. 5.1(a), the magnetic primitive unit cell of the crystalline silicon immersed in the uniform magnetic field has q lattice points. Correspondingly, $8q$ electrons are contained in the magnetic primitive unit cell. If the system has N_{t_n} points of t_n , then the number of electrons in the whole system is $8qN_{t_n}$.

As mentioned in the above, the magnetic first Brillouin zone has N_{t_n} allowed points of k , so that the $8q$ bands below the energy gap that exist around -6 eV are valance bands, and the higher bands are conduction bands. Using this facts, it is also confirmed in Fig. 5.5(a) that the original energy gap of the crystalline silicon, which ranges from about -6.5 eV to -5.3 eV at $p/q=0$, remains up to the magnitude of the magnetic field, $p/q=0.2$. This would be due to the both the increase of the top of the valance band and the decrease of the bottom of the conduction band that are mainly caused by the Zeeman term.

Chapter 6

Application to simple cubic lattice immersed in the uniform magnetic field

In this chapter, the dHvA oscillation is revisited by means of the MFRTB method. Furthermore, the validity of the LK formula, which is commonly used for investigating the dHvA oscillation, is also checked. For this aim, the MFRTB method is applied to the simple cubic lattice immersed in the uniform magnetic field. The reason why a hypothetical simple cubic lattice is chosen as a test system is that the extremal cross-section of the Fermi surface can be obtained exactly, which enables us to check the validity of the LK formula.

6.1 Expression for the simultaneous equations

Consider the simple cubic lattice immersed in the uniform magnetic field, the magnitude of which is given by Eq. (4.2). In this system, we suppose that each lattice point has one atom with one s -electron. In simple cubic lattice, the nearest neighbor atoms are six having coordinates $\mathbf{T}_W = (0, a, 0), (0, -a, 0), (a, 0, 0), (-a, 0, 0), (0, 0, a)$ and $(0, 0, -a)$ respectively, with $W = 1, 2, \dots, 6$. By utilizing the magnetic Bloch theorem that comes from the translational symmetry in the uniform magnetic field [38], we have the relation between the expansion coefficients in the similar way to the previous cases (Chapters 4 and 5). The translational vector \mathbf{t}_n and wave vector \mathbf{k} for the simple cubic lattice immersed in the uniform magnetic field are defined by

$$\mathbf{t}_n = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3, \quad (6.1)$$

and

$$\mathbf{k} = k_1 \mathbf{b}_1 + k_2 \mathbf{b}_2 + k_3 \mathbf{b}_3 \quad (6.2)$$

respectively, where $n_1, n_2,$ and n_3 are integers, and $k_1, k_2,$ and k_3 are real numbers ranging from -0.5 to 0.5 . From Eq. (6.1) the ‘magnetic primitive cell’ is defined by three primitive

vectors:

$$\mathbf{a}_1 = a\mathbf{e}_x, \quad \mathbf{a}_2 = qa\mathbf{e}_y \quad \text{and} \quad \mathbf{a}_3 = a\mathbf{e}_z, \quad (6.3)$$

and the corresponding ‘magnetic reciprocal lattice’ is constructed by the following magnetic reciprocal lattice vectors [Eq. (6.2)] as

$$\mathbf{b}_1 = \frac{2\pi}{a}\mathbf{e}_x, \quad \mathbf{b}_2 = \frac{2\pi}{qa}\mathbf{e}_y \quad \text{and} \quad \mathbf{b}_3 = \frac{2\pi}{a}\mathbf{e}_z \quad (6.4)$$

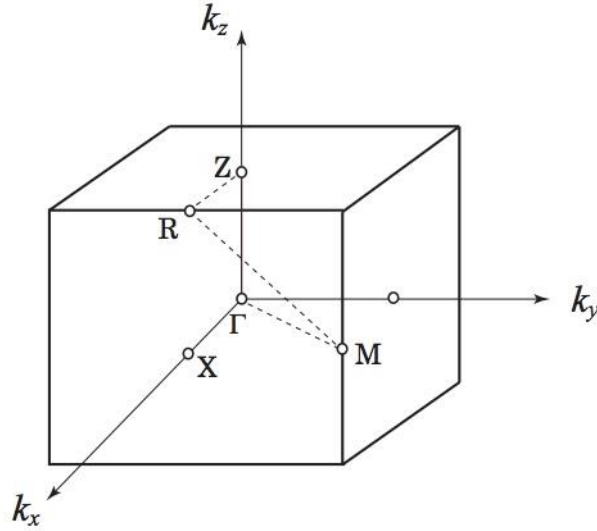


Fig. 6.1 Magnetic first Brillouin zone for simple cubic lattice immersed in the uniform magnetic field, together with some symmetry points $\Gamma = \frac{2\pi}{a}(0,0,0)$; $Z = \frac{2\pi}{a}(0,0,0.5)$; $R = \frac{2\pi}{a}(0.5,0,0.5)$; $X = \frac{2\pi}{a}(0.5,0,0)$; and $M = \frac{2\pi}{a}(0.5,0.5/q,0)$ [54].

We consider only the hopping integrals between the nearest neighbor atoms as done in the usual TB method [55]. Taking into consideration relativistic atomic orbitals with $(n, \ell, J, M) = (n, 0, 1/2, \pm 1/2)$, we can calculate the matrix elements of Hamiltonian, i.e., Eq. (3.71), and get the simultaneous equations for the expansion coefficients as

$$\left[\bar{\varepsilon}_{n'0\frac{1}{2}}(\mathbf{B}=0) + \Delta \bar{\varepsilon}_{n'0\frac{1}{2}M'}(\mathbf{B}=0) + \frac{eB}{m} \hbar M' + 2K_1 \left(n'0\frac{1}{2}, n'0\frac{1}{2} \right)_{1/2} [\cos(2\pi k_3) + \cos\{2\pi(k_1 + \frac{p}{q}I')\}] \right] C_k^{n'0\frac{1}{2}M'}(I'\mathbf{a}_2) + K_1 \left(n'0\frac{1}{2}, n'0\frac{1}{2} \right)_{1/2} \times \left[C_k^{n'0\frac{1}{2}M'}\{(I'+1)\mathbf{a}_2\} + C_k^{n'0\frac{1}{2}M'}\{(I'-1)\mathbf{a}_2\} \right] = E_k C_k^{n'0\frac{1}{2}M'}(I'\mathbf{a}_2). \quad (6.5)$$

The matrix form of Eq. (6.5) is same as Eq. (4.34). Only the difference is that the diagonal elements $S_0, S'_0, S_1, \dots, S_{q-1}, S'_{q-1}$ are changed by the additional factor $\cos(2\pi k_3)$. Because

of considering the monoatomic crystal, the dependences of $\bar{\varepsilon}_{n'0\frac{1}{2}}(\mathbf{B}=0)$, $\Delta\bar{\varepsilon}_{n'0\frac{1}{2}M'}(\mathbf{B}=0)$, $K_1\left(n'0\frac{1}{2}, n'0\frac{1}{2}\right)_{1/2}$, and $C_k^{n'0\frac{1}{2}M'}$ on a_i is omitted. By solving the simultaneous equations, we have $2q$ eigenvalues for each \mathbf{k} , and obtain $E - \mathbf{k}$ curves in the presence of the uniform magnetic field. Since the magnitude of relativistic TB parameters never affect the discussions on the validity of the LK formula, we here also use the same values as we used in the previous Chapter 4. i.e.,

$$\bar{\varepsilon}_{n'0\frac{1}{2}}(\mathbf{B}=0) + \Delta\bar{\varepsilon}_{n'0\frac{1}{2}M'}(\mathbf{B}=0) = -12.1538 \text{ (eV)} \quad \text{and} \quad K_1\left(n'0\frac{1}{2}, n'0\frac{1}{2}\right)_{1/2} = -1.7391 \text{ (eV)}. \quad (6.6)$$

6.2 Results and discussions

6.2.1 Electronic structures for the simple cubic lattice immersed in the uniform magnetic field

Figure 6.2(a) shows $E - \mathbf{k}$ curves of the simple cubic lattice immersed in the uniform magnetic field where the values of p and q are fixed at 10 and 401, respectively. Symbols in the horizontal axis corresponds to the special \mathbf{k} -points in the magnetic first Brillion zone that is drawn in Fig. 6.1.

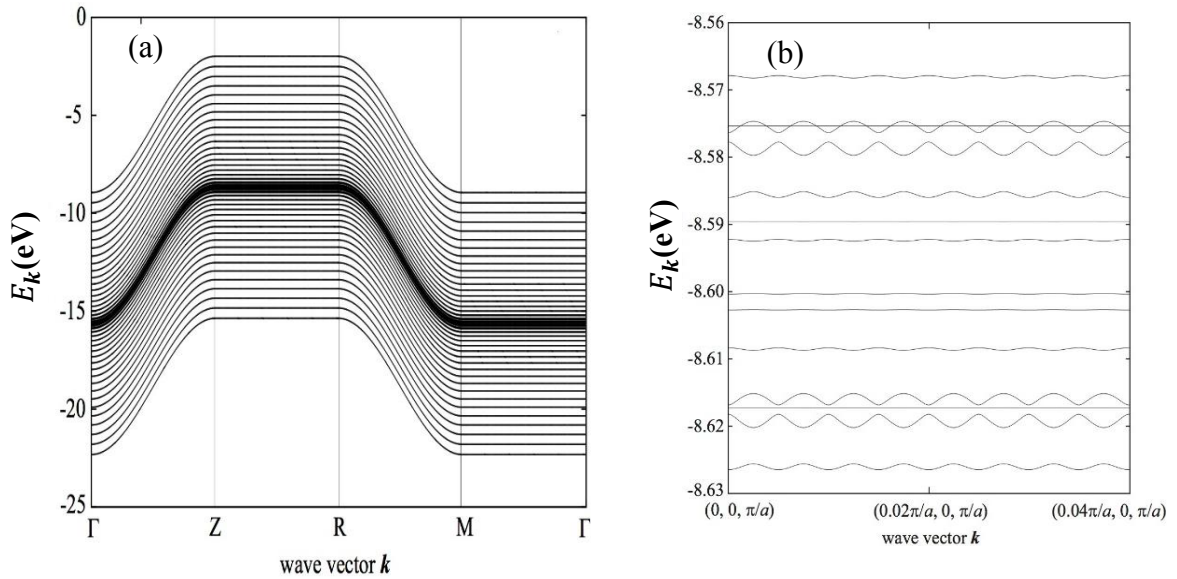


Fig. 6.2 (a) $E - \mathbf{k}$ curves for the simple cubic lattice immersed in the uniform magnetic field of $(p/q) = (10,401)$. (b) The magnified view of (a) along the ZR-line [54].

It is found from Fig. 6.2(a) that the energy little depends on the components of the wave vector perpendicular to the magnetic field (i.e. k_x and k_y) and varies with the component parallel to the magnetic field (i.e. k_z). This means that the motion of electrons in the plane perpendicular to the magnetic field is essentially changed due to the Lorentz force. On the other hand, since the electron is not subjected to the Lorentz force in the z -direction, $E - \mathbf{k}$ curves remain with relatively large bandwidth. Seeing the $E - \mathbf{k}$ curves macroscopically, they are positioned in the form of parallel lines with some energy spacing to each other, which seemingly looks like the Landau levels. However, as shown in Fig. 6.2(b), each energy band has a small but definite width, which is hereafter called the fine structure of the $E - \mathbf{k}$ curves [56]. Macroscopical shapes of the $E - \mathbf{k}$ curves would come from the fact that the orbital quantization contained in the LK formula inevitably emerges also in the calculation results of the MFRTB method, while the fine structure of the $E - \mathbf{k}$ curves is due to the periodic potential of the crystal [38].

Figure 6.3(a) shows the dependence of the energy spectrum on the magnitude of the magnetic field in the case where the wave vector is restricted in the plane perpendicular to the magnetic field. In this calculation, p changes from 1 to 401 with fixing q at 401. The characteristic gap structures, which are similar to Hofstadter's butterfly diagram [8], can be seen in Fig. 6.3(a). On the other hand, the characteristic gap structures are not found when the wave vector varies along the axis parallel to the magnetic field [Fig. 6.3(b)]. This is due to the strong dependence of the electron energy on k_z , which is shown in Fig. 6.2(a).

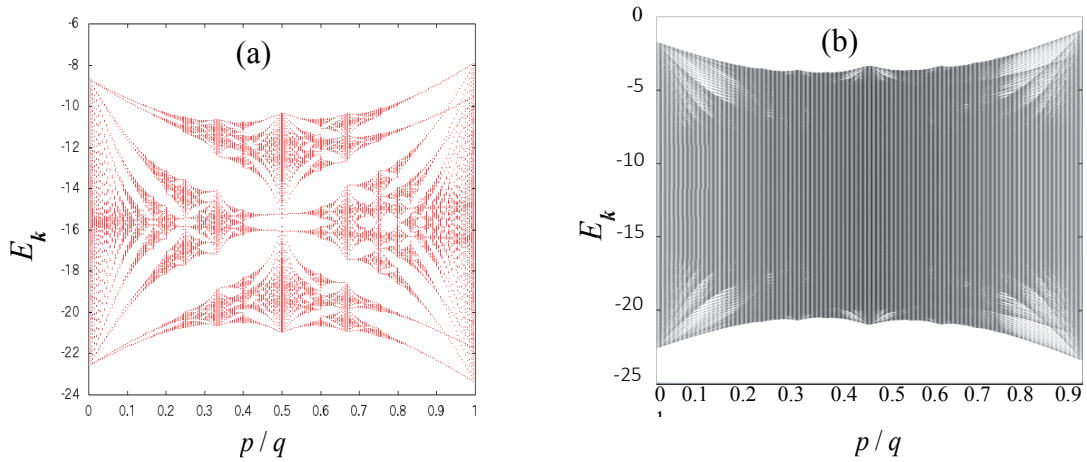


Fig. 6.3 Energy spectrum as a function of magnitude of magnetic field (a) in the case of varying wave vectors in the $k_x - k_y$ plane of the magnetic first Brillouin zone and (b) in the case of varying wave vectors along the k_z axis of the magnetic first Brillouin zone [54].

In addition, the energy diagram shown in Fig. 6.3(a) and 6.3(b) split into two parts, which is due to the Zeeman term of Eq. (6.5). As can be seen in Fig. 6.3(a), the magnitude of such splitting becomes large as the magnetic field increases. Thus, the MFRTB method is regarded as the generalized method that includes Hofstadter's method [8].

6.2.2 Density of states (DOS)

In order to show the oscillation of the total energy of the system immersed in a uniform magnetic field, we first calculate the DOS of the system. For this purpose, we use the theorem that has been discussed in previous chapter [Chapter 5]. We suppose that the number of magnetic primitive unit cells contained in the system is denoted by N_{t_n} . Since the volume of the magnetic primitive cell is given by qa^3 from Eq. (6.3), the volume of the system is equal to $N_{t_n}qa^3$. According to theorem, there are N_{t_n} number of \mathbf{k} -points in the magnetic first Brillion zone. This assumption would be reasonable because \mathbf{k} -points are distributed uniformly in the limit of zero magnetic field. Under this assumption, we calculate $E_{\mathbf{k}}$ for each \mathbf{k} -point and calculate the total number of energy levels less than the energy ε , i.e., $N(\varepsilon)$. We obtain the DOS, $D(\varepsilon)$ by differentiating $N(\varepsilon)$ with respect to ε , and by dividing it by the volume of the system $N_{t_n}qa^3$.

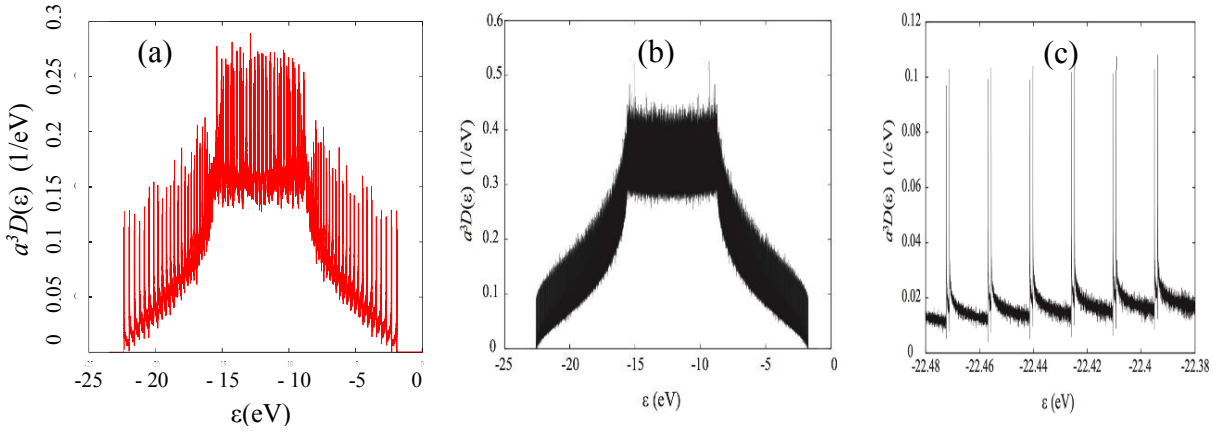


Fig. 6.4 Density of states in the case of (a) $(p/q) = (1, 53)$ ($\mathbf{B} = 264.71\text{T}$); (b) $(p/q) = (1, 1399)$ ($\mathbf{B} = 7.253\text{T}$) and (c) Magnified view of (b) [54].

The DOSs for the simple cubic lattice immersed in a uniform magnetic field are shown in Figs. 6.4(a) and 6.4(b) for the cases of $(p, q) = (1, 53)$ and $(p, q) = (1, 1399)$ respectively. Figure 6.4(c) is the magnified view of Fig. 6.4(b). The value of N_{t_n} , which is used in actual calculations, is determined by requiring that the dependence of the total energy per unit volume on the size of the system is negligibly small. In these calculations, we take $8q^2 \times 10^6$ [57] as N_{t_n} . It is found from Figs. 6.4(a), 6.4(b) and 6.4(c) that the DOS is analogous to that of the free electron immersed in the uniform magnetic field [58]. Namely, the DOS consists of two characteristic parts. One comes from $E - \mathbf{k}$ curves along the k_z axis, the shape of which looks like trapezoid that corresponds to the DOS of the simple cubic lattice for the zero magnetic field. The other comes from discretized energy levels, the shape of which looks like the delta function. It is also found

in Fig. 6.4(c) that there are two types of energy splits. The large energy splitting corresponds to the orbital quantization, and the small one is due to the spin Zeeman splitting.

6.2.3 Revisit of the dHvA effect via the MFRTB method

In order to calculate the total energy, the Fermi energy must be estimated. In the present model system, one lattice point has one atom with one s -electron, so that there exists one electron in each lattice points. Since it has q lattice points, the magnetic primitive unit cell contains q -electrons. Since N_{t_n} magnetic primitive unit cells are contained in the system, we can say that the total number electrons in the model system are given by qN_{t_n} . According to the theorem mentioned in the previous subsection, the total number of \mathbf{k} -points is equal to N_{t_n} . Since $2q$ energy levels are calculated for each \mathbf{k} -points, totally $2qN_{t_n}$ energy levels are obtained in the magnetic first Brillion zone. Therefore, the lower half of the energy levels are occupied by electrons, which corresponds to the valence bands. Using this fact, the Fermi energy can be estimated.

Figures 6.5(a) and 6.5(b) show the dependence of the total energy (E_{total}) on the inverse of the magnetic field ranging from 9.78 to 9.90 (T) [Fig. 6.5(a)] and from 43.5 to 45.7 (T) [Fig. 6.5(b)] respectively. Oscillatory behavior of the total energy with respect to the magnetic field is clearly observed. The magnetization can be calculated by taking the differential of the total energy with respect to the magnetic field, where we use the cubic spline interpolation technique. The magnetic-field-dependences of the magnetization [$M(B)$] are shown in Figs. 6.6(a) and 6.6(b). In Fig. 6.6(b), some small peaks of the magnetization can be found in addition to the global oscillation. Hereafter, we discuss the global oscillation of the magnetization. Concerning the small peaks, we will discuss in the subsequent subsection.

The period of the global oscillation of the magnetization can be calculated by the Fourier transformation of the waveform of the magnetization. The evaluated values of periods corresponding to Figs. 6.6(a) and 6.6(b) are $3.87 \times 10^{-4} (1/T)$ and $3.85 \times 10^{-4} (1/T)$ respectively (Table-VI).

Table-VI. Periods of the oscillation of the magnetization.

Magnetic field (B)	Period (1/T)	
	MFRTB Method	LK formula
9.78–9.90 (T)	3.87×10^{-4}	3.858×10^{-4}
43.50–45.70 (T)	3.85×10^{-4}	3.858×10^{-4}
538.69–3328 (T)	3.98×10^{-4}	3.858×10^{-4}

On the other hand, according to the LK formula, the period of the oscillation of the magnetization is related to the extremal cross-sectional area of the Fermi surface A_{ext} for

zero magnetic field system, which is given by

$$\Delta\left(\frac{1}{B}\right) = \frac{2\pi|e|}{\hbar A_{ext}} \quad (6.7)$$

In the case of simple cubic lattice, the extremal cross-sectional area of the Fermi surface exists at the boundary of the Brillion zone [53]. Two kinds of Fermi surface exist; one is the electron sheet that is centered at X-point of the Brillion zone [59], and the other is the hole sheet that is centered at the M-point of the Brillion zone [59]. They have the same cross-sectional areas ($A_{ext} = 0.248582 \times 10^{-20} m^{-2}$), which results in the degenerate magnetic oscillations of the dHvA effect. The sizes of the Fermi surface sheets are dependent on the TB parameters of the zero magnetic field.

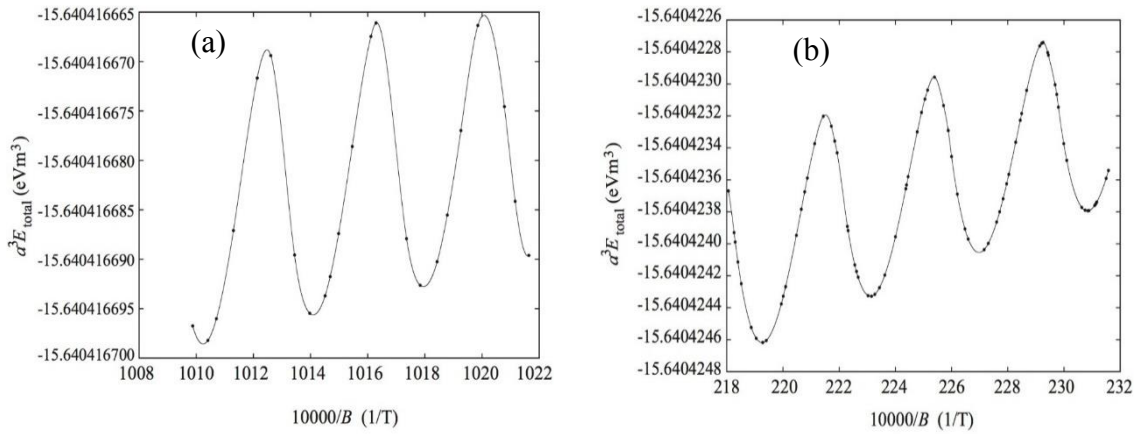


Fig. 6.5 Oscillation of total energy with inverse magnetic field (a) B varies from 9.78T – 9.90T and (b) B varies from 43.5T – 45.7T [54].

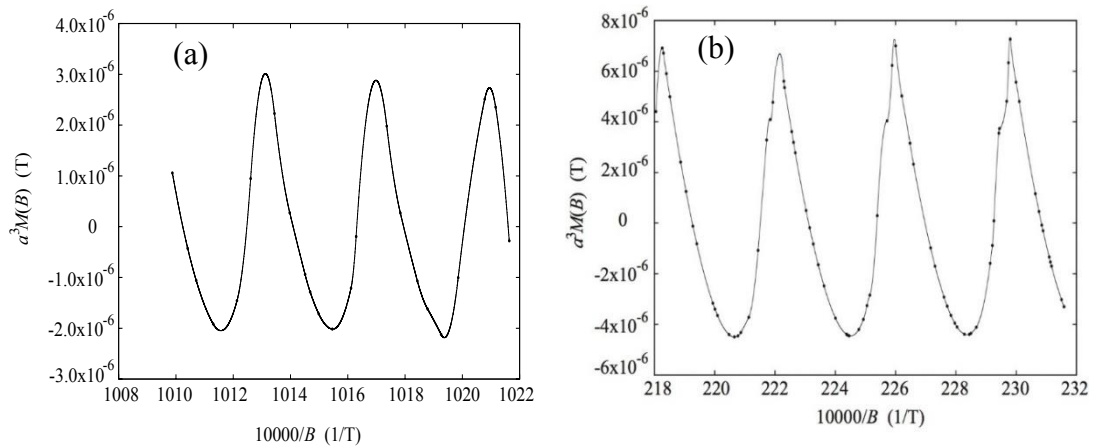


Fig. 6.6 Dependence of magnetization on the inverse of the magnitude of the magnetic field (a) B varies from 9.78T – 9.90T and (b) B varies from 43.5T – 45.7T [54].

The use of the same values as Eq. (6.6) allows comparison of the results of the LK formula with those of the MFRTB method. Using Eq. (6.7), the period of the LK formula is estimated as $3.858 \times 10^{-4} (1/T)$, which is quite close to the periods that are obtained from the MFRTB method (Table-VI). This means that the LK formula, which is based on the Bohr-Sommerfeld quantization rule and semi classical equation of motion, is a good approximation in the magnetic field less than about 46 (T).

6.2.4 Additional oscillation peaks of the magnetization

As mentioned in the previous subsection, some small peaks of the magnetization can be found in Fig. 6.6(b) in addition to the global oscillation that is consistent with the conventional LK formula. Taking into consideration the fact that the LK formula relates the origin of the magnetic oscillation with the extremal cross-section of the Fermi surface, additional oscillation peaks of the magnetization cannot be explained by the LK formula. These additional peaks are thought to be due to the effect of the periodic potential of the crystal. This is because the Landau levels, which are obtained for the case of zero periodic potential, do not cause such additional oscillation peaks of the magnetization [32,34]. The periodic potential of the crystal also results in the fine structure of $E - \mathbf{k}$ curves that is shown in Fig. 6.2(b). Therefore, fine structure would produce additional oscillation peaks that cannot be related to the Fermi surface via the LK formula. Furthermore, the effect of the energy band widening in $k_x - k_y$ plane, which corresponds to the fine structure of $E - \mathbf{k}$ curves, becomes remarkable in the high magnetic field due to the increase of the electron hopping between the electronic states with the magnitude of the magnetic field [38]. This is the reason why the additional oscillation peaks of the magnetization are clearly seen in Fig. 6.6(b), while they are not clearly seen in Fig. 6.6(a). Of course, it is expected that the number of small peaks may appear in the magnetization curve if the intervals of the magnetic field are narrowed in the calculations

6.3 Extremely high magnetic field

For reference, we shall consider the case of the extremely high magnetic field. In the extremely high magnetic field ranging from 538.69 (T) to 3328 (T), the magnetic oscillations of the total energy and magnetization are calculated as shown in Figs. 6.7(a) and 6.7(b), respectively. The magnified view of Fig. 6.7(b) is shown in Fig. 6.7(c). Additional oscillation peaks, which are discussed in the previous subsection, are found in Fig. 6.7(b) more clearly than in Fig. 6.6(b). Another noticeable thing in the extremely high magnetic field is that the period of the global oscillation increases. Specifically, it is estimated as $3.98 \times 10^{-4} (1/T)$, which deviates from the LK formula by about 3% (Table-VI). This would possibly be caused by the limit of the validity of the LK formula. We shall discuss the reason below.

As mentioned in Chapter 1, the LK formula is based on the Bohr-Sommerfeld quanti-

zation rule that is valid for the energy levels with fairly high quantum number [37]. The maximum quantum number is roughly estimated by the ratio $\varepsilon_F / \hbar\omega_c$, where ε_F and ω_c are the Fermi energy and cyclotron frequency, respectively [37]. This ratio becomes the order of 10^3 in the case of $B \sim 10$ (T), in which case the results of the MFRTB method certainly agree with those calculated from the LK formula, as mentioned in the previous subsection. On the other hand, in the case of $B \sim 10^3$ (T), the ratio is about 10, which seems to be too small for the correctness of the Bohr-Sommerfeld quantization rule, as expected from the present results (Table-VI).

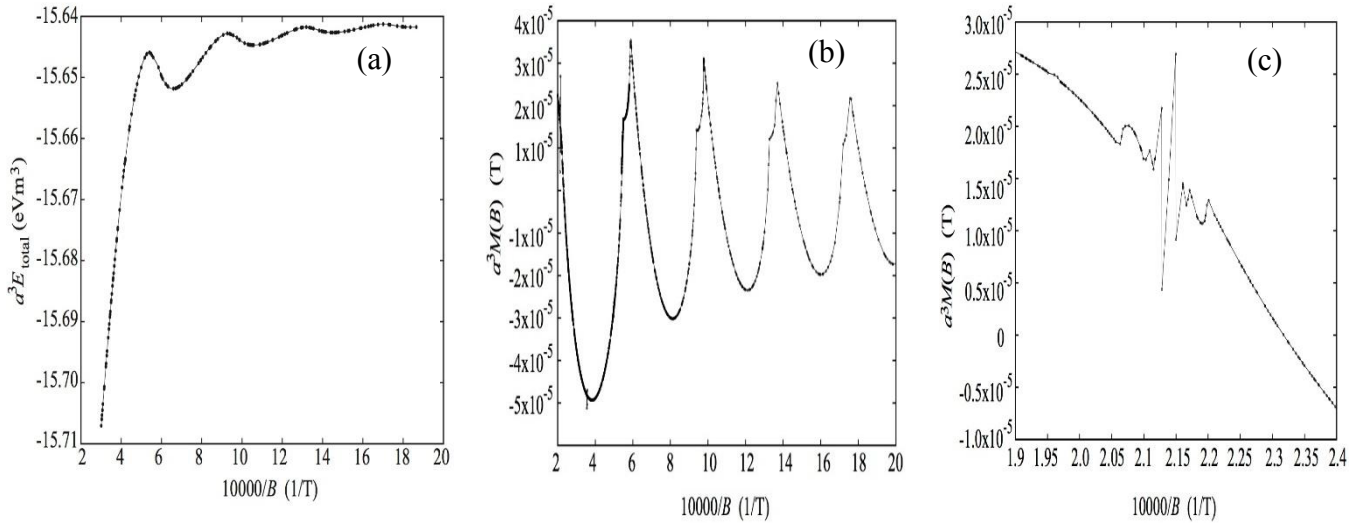


Fig. 6.7 Oscillation of the (a) total energy and (b) magnetization on the inverse of the magnitude of the magnetic field where B varies from 538.69T – 3328T. Magnified view of (b) is shown in (c) [54].

The ratio $\varepsilon_F / \hbar\omega_c$ may become a practical and quantitative indication of whether the LK formula holds well or not. It should be noted that the Fermi energy generally increases with the electron density. Therefore there is possibility that the incorrectness of the LK formula would become obvious even magnetic field less than 10^3 (T) for the metallic system with the low electron density.

Chapter 7

Conclusions

We develop the MFRTB method, which is the first principles calculation method for electronic structures of materials immersed in the uniform magnetic field. In this method, both magnetic field and relativistic effects are taken into consideration by treating the Dirac equation for an electron that moves in the both magnetic field and periodic potential of a crystal. The striking features of the MFRTB method are as follows

- (1) The MFRTB method is applicable to the electronic structure calculations of actual crystalline materials immersed in the uniform magnetic field.
- (2) It is also shown that within the lowest order perturbation theory, the magnetic hopping integrals are approximated as the relativistic hopping integrals multiplied by the Peierls phase factor. This approximation for the magnetic hopping integrals can be improved systematically by incorporating higher order correction terms.
- (3) We develop the relativistic version of Slater-Koster table in order to calculate the relativistic hopping integrals. Specially, the explicit form of 64 kinds of relativistic hopping integrals are given by the linear combination of relativistic TB parameters. The relativistic TB parameters can be readily obtained from the electronic structure calculations for the zero magnetic field case.

In order to check the validity and feasibility of the MFRTB method, we apply this method to two systems. One is the two-dimensional square lattice immersed in the uniform magnetic field, and other is the crystalline silicon immersed in the uniform magnetic field.

- (4) The application of the MFRTB method to the two-dimensional lattice immersed in the uniform magnetic field is described in Chapter 4, and it is shown that the MFRTB method includes the Hofstadter's method [8]. Namely, if the Zeeman term is neglected, then the MFRTB method reproduces so-called Hofstadter's butterfly diagram.
- (5) The application of the MFRTB method to the crystalline silicon immersed in the uniform magnetic field is described in Chapter 5. We successfully revealed E - \mathbf{k} curves of the crystalline silicon immersed in the uniform magnetic field at the first time. Furthermore, recursive structures in the magnetic-field-dependent energy diagram, i.e., the butterfly patterns, can be seen in the $k_x - k_y$ plane of the magnetic first Brillouin zone [Figs. 5.7(b) and 5.7(c)]. Recursive structures are expected to be observed by the experiments in an appropriate system such as the Si/SiC heterostructure.

(6) It is also found in Chapter 5 that the widths of the energy bands in the $k_x - k_y$ plane increases with the magnitude of magnetic field [Figs. 5.6(a) – 5.6(e)]. This suggest that the useful range of the effective mass approximation, which leads to the Landau levels, is limited to the limit of the low magnetic field.

In order to show the availability of the MFRTB method, in Chapter 6, we apply the MFRTB method to the simple cubic lattice immersed in the uniform magnetic field in order to revisit the dHvA effect by means of MFRTB method.

(7) Oscillations of the total energy and magnetization (dHvA effect) are successfully revisited by the MFRTB method. Although the conventional LK formula for the dHvA effect is a good approximation in experimentally available magnetic field (around 9.8T to 46T), the MFRTB method is capable of becoming a useful method to describe the magnetic oscillations without assumptions contained in the LK formula.

(8) Especially in the high magnetic field, additional oscillation peaks of the magnetization, which cannot be explained by LK formula, are found by MFRTB method. These additional magnetic oscillation peaks may come from the fine structure of $E - \mathbf{k}$ curves, which is first revealed through the MFRTB method.

(9) The present work may become an important milestone toward revisiting the dHvA oscillations of more realistic lattice structures by means of the MFRTB method. For example, when we apply the MFRTB method to more realistic lattice structures, magnetic oscillations will be obtained in a similar way to the present case (a simple cubic lattice). Namely, by reference to the above-mentioned knowledge obtained from the present work, the LK formula is expected to give a good approximation for the period of the main oscillation in the low magnetic field region. Therefore, if there is a discrepancy between the period that is calculated by the MFRTB method and that of the LK formula, it can be concluded that this discrepancy comes from the error of the extremal cross-section of the Fermi surface. Also, if additional fine oscillations besides the main oscillation are observed in experiments, we can say that such fine oscillations do not always come from the errors of the extremal cross-section of the calculated Fermi surface but may come from the fine structures of $E - \mathbf{k}$ curves obtained from the MFRTB method.

Thus we successfully obtain the first principle method, i.e., MFRTB method, which is applicable to actual crystalline materials immersed in the uniform magnetic field. This method is expected to be useful to describe the phenomena that are related to the magnetic Bloch electrons.

Appendix: A

Show that the matrix elements of Hamiltonian is Hermitian

$$\text{i.e. } H_{(n'l'JM')j,(n\ell JM)i}^\dagger = H_{(n\ell JM)i,(n'l'JM')j}.$$

Proof:

The matrix elements of Hamiltonian given in Eq. (2.13), is

$$H_{(n'l'JM')j,(n\ell JM)i} = \sum_{\mathbf{R}_n} e^{ik \cdot (\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j)} t_{n'l'JM',n\ell JM}^{a_j a_i}(\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j), \quad (\text{A1})$$

where the relativistic hopping integral is defined as [Eq. (2.21)]

$$t_{n'l'JM',n\ell JM}^{a_j a_i}(\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j) = \int \varphi_{n'l'JM'}^{a_j}(\mathbf{r})^\dagger \left\{ \frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right\} \varphi_{n\ell JM}^{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j) d^3 r. \quad (\text{A2})$$

Similarly, the relativistic hopping integral at position $\{-(\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j)\}$ is

$$t_{n\ell JM,n'l'JM'}^{a_i a_j}\{-(\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j)\} = \int \varphi_{n\ell JM}^{a_i}(\mathbf{r})^\dagger \left\{ \frac{V_{a_i}(\mathbf{r}) + V_{a_j}(\mathbf{r} + \mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j)}{2} \right\} \varphi_{n'l'JM'}^{a_j}(\mathbf{r} + \mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j) d^3 r. \quad (\text{A3})$$

Taking the complex conjugate of Eq. (A3), we have

$$t_{n\ell JM,n'l'JM'}^{a_i a_j}\{-(\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j)\}^* = \int \varphi_{n\ell JM}^{a_i}(\mathbf{r})^t \left\{ \frac{V_{a_i}(\mathbf{r}) + V_{a_j}(\mathbf{r} + \mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j)}{2} \right\} \varphi_{n'l'JM'}^{a_j}(\mathbf{r} + \mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j)^* d^3 r.$$

Changing the variable $\mathbf{r}' = \mathbf{r} + \mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j$, then

$$= \int \varphi_{n\ell JM}^{a_i}(\mathbf{r}' - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)' \left\{ \frac{V_{a_i}(\mathbf{r}' - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j) + V_{a_j}(\mathbf{r}')}{2} \right\} \varphi_{n'\ell'JM'}^{a_j}(\mathbf{r}')^* d^3 r.$$

Again changing the variable $\mathbf{r}'' = \mathbf{r}' - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j$, then

$$\begin{aligned} &= \int \left[\varphi_{n\ell JM}^{a_i}(\mathbf{r}'')^1 \quad \varphi_{n\ell JM}^{a_i}(\mathbf{r}'')^2 \quad \varphi_{n\ell JM}^{a_i}(\mathbf{r}'')^3 \quad \varphi_{n\ell JM}^{a_i}(\mathbf{r}'')^4 \right] \left\{ \frac{V_{a_i}(\mathbf{r}'') + V_{a_j}(\mathbf{r}')}{2} \right\} \\ &\quad \times \begin{bmatrix} \varphi_{n'\ell'JM'}^{a_j}(\mathbf{r}')^{*1} \\ \varphi_{n'\ell'JM'}^{a_j}(\mathbf{r}')^{*2} \\ \varphi_{n'\ell'JM'}^{a_j}(\mathbf{r}')^{*3} \\ \varphi_{n'\ell'JM'}^{a_j}(\mathbf{r}')^{*4} \end{bmatrix} d^3 r. \\ &= \int \left[\varphi_{n\ell JM}^{a_i}(\mathbf{r}'')^1 \varphi_{n'\ell'JM'}^{a_j}(\mathbf{r}')^{*1} + \varphi_{n\ell JM}^{a_i}(\mathbf{r}'')^2 \varphi_{n'\ell'JM'}^{a_j}(\mathbf{r}')^{*2} + \varphi_{n\ell JM}^{a_i}(\mathbf{r}'')^3 \varphi_{n'\ell'JM'}^{a_j}(\mathbf{r}')^{*3} \right. \\ &\quad \left. + \varphi_{n\ell JM}^{a_i}(\mathbf{r}'')^4 \varphi_{n'\ell'JM'}^{a_j}(\mathbf{r}')^{*4} \right] \left\{ \frac{V_{a_i}(\mathbf{r}'') + V_{a_j}(\mathbf{r}')}{2} \right\} d^3 r, \\ &= \int \left[\varphi_{n'\ell'JM'}^{a_j}(\mathbf{r}')^{*1} \varphi_{n\ell JM}^{a_i}(\mathbf{r}'')^1 + \varphi_{n'\ell'JM'}^{a_j}(\mathbf{r}')^{*2} \varphi_{n\ell JM}^{a_i}(\mathbf{r}'')^2 + \varphi_{n'\ell'JM'}^{a_j}(\mathbf{r}')^{*3} \varphi_{n\ell JM}^{a_i}(\mathbf{r}'')^3 \right. \\ &\quad \left. + \varphi_{n'\ell'JM'}^{a_j}(\mathbf{r}')^{*4} \varphi_{n\ell JM}^{a_i}(\mathbf{r}'')^4 \right] \left\{ \frac{V_{a_i}(\mathbf{r}'') + V_{a_j}(\mathbf{r}')}{2} \right\} d^3 r, \\ &= \int \left[\varphi_{n'\ell'JM'}^{a_j}(\mathbf{r}')^{*1} \quad \varphi_{n'\ell'JM'}^{a_j}(\mathbf{r}')^{*2} \quad \varphi_{n'\ell'JM'}^{a_j}(\mathbf{r}')^{*3} \quad \varphi_{n'\ell'JM'}^{a_j}(\mathbf{r}')^{*4} \right] \left\{ \frac{V_{a_i}(\mathbf{r}'') + V_{a_j}(\mathbf{r}')}{2} \right\} \\ &\quad \times \begin{bmatrix} \varphi_{n\ell JM}^{a_i}(\mathbf{r}'')^1 \\ \varphi_{n\ell JM}^{a_i}(\mathbf{r}'')^2 \\ \varphi_{n\ell JM}^{a_i}(\mathbf{r}'')^3 \\ \varphi_{n\ell JM}^{a_i}(\mathbf{r}'')^4 \end{bmatrix} d^3 r. \\ &= \int \varphi_{n'\ell'JM'}^{a_j}(\mathbf{r}')^\dagger \left\{ \frac{V_{a_j}(\mathbf{r}') + V_{a_i}(\mathbf{r}'')}{2} \right\} \varphi_{n\ell JM}^{a_i}(\mathbf{r}'') d^3 r. \end{aligned}$$

Again changing the variable $\mathbf{r}'' = \mathbf{r}' - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j$, then

$$= \int \varphi_{n'\ell'JM'}^{a_j}(\mathbf{r}')^\dagger \left\{ \frac{V_{a_j}(\mathbf{r}') + V_{a_i}(\mathbf{r}' - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right\} \varphi_{n\ell JM}^{a_i}(\mathbf{r}' - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j) d^3 r,$$

Finally, changing the variable $\mathbf{r}' = \mathbf{r}$, then

$$\begin{aligned}
&= \int \varphi_{n'\ell'JM'}^{a_j}(\mathbf{r})^\dagger \left\{ \frac{V_{a_j}(\mathbf{r}) + V_{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)}{2} \right\} \varphi_{n\ell JM}^{a_i}(\mathbf{r} - \mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j) d^3r, \\
&= t_{n\ell JM, n'\ell'JM'}^{a_j a_i}(\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j)
\end{aligned} \tag{A4}$$

Also we have

$$\begin{aligned}
H_{(n'\ell'JM')j, (n\ell JM)i}^\dagger &= H_{(n\ell JM)i, (n'\ell'JM')j}^* \\
&= \sum_{\mathbf{R}_n} e^{-ik \cdot (-\mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)} t_{n\ell JM, n'\ell'JM'}^{a_i a_j}(-\mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)^* \\
&= \sum_{\mathbf{R}_{n'}} e^{ik \cdot (\mathbf{R}_{n'} + \mathbf{d}_i - \mathbf{d}_j)} t_{n\ell JM, n'\ell'JM'}^{a_i a_j}(-\mathbf{R}_{n'} - \mathbf{d}_i + \mathbf{d}_j)^*
\end{aligned}$$

Changing the variable $\mathbf{R}_{n'} = \mathbf{R}_n$, then

$$= \sum_{\mathbf{R}_n} e^{ik \cdot (\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j)} t_{n\ell JM, n'\ell'JM'}^{a_i a_j}(-\mathbf{R}_n - \mathbf{d}_i + \mathbf{d}_j)^*. \tag{A5}$$

Substituting Eq. (A4) into Eq. (A5), we have

$$H_{(n'\ell'JM')j, (n\ell JM)i}^\dagger = \sum_{\mathbf{R}_n} e^{ik \cdot (\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j)} t_{n'\ell'JM', n\ell JM}^{a_j a_i}(\mathbf{R}_n + \mathbf{d}_i - \mathbf{d}_j)$$

$$H_{(n'\ell'JM')j, (n\ell JM)i}^\dagger = H_{(n'\ell'JM')j, (n\ell JM)i}$$

Hence the matrix element of Hamiltonian is Hermitian.

Appendix: B

Definition of spherical harmonics

- i. $Y_{0,0}(\theta, \phi) = C_s(\theta, \phi)$
- ii. $Y_{1,0}(q, f) = C_z(q, f)$
- iii. $Y_{1,1}(q, f) = -\frac{1}{\sqrt{2}} \hat{e} C_x(q, f) + i C_y(q, f) \hat{u}$
- iv. $Y_{1,-1}(q, f) = \frac{1}{\sqrt{2}} \hat{e} C_x(q, f) - i C_y(q, f) \hat{u}$
- v. $Y_{2,0}(q, f) = C_{3z^2-r^2}(q, f)$
- vi. $Y_{2,1}(q, f) = -\frac{1}{\sqrt{2}} \hat{e} C_{xz}(q, f) + i C_{yz}(q, f) \hat{u}$
- vii. $Y_{2,-1}(q, f) = \frac{1}{\sqrt{2}} \hat{e} C_{xz}(q, f) - i C_{yz}(q, f) \hat{u}$
- viii. $Y_{2,2}(q, f) = \frac{1}{\sqrt{2}} \hat{e} C_{x^2-y^2}(q, f) + i C_{xy}(q, f) \hat{u}$
- ix. $Y_{2,-2}(q, f) = \frac{1}{\sqrt{2}} \hat{e} C_{x^2-y^2}(q, f) - i C_{xy}(q, f) \hat{u}$

Definition cubic harmonics:

- x. $C_s(q, f) = Y_{0,0}(q, f)$
- xi. $C_z(q, f) = Y_{1,0}(q, f)$
- xii. $C_x(q, f) = \frac{1}{\sqrt{2}} \hat{e} Y_{1,-1}(q, f) - Y_{1,1}(q, f) \hat{u}$
- xiii. $C_y(q, f) = \frac{i}{\sqrt{2}} \hat{e} Y_{1,-1}(q, f) + Y_{1,1}(q, f) \hat{u}$

- xiv. $C_{3z^2-r^2}(q, f) = Y_{2,0}(q, f)$
- xv. $C_{yz}(q, f) = \frac{i}{\sqrt{2}} \{ Y_{2,-1}(q, f) + Y_{2,1}(q, f) \}$
- xvi. $C_{xz}(q, f) = \frac{1}{\sqrt{2}} \{ Y_{2,-1}(q, f) - Y_{2,1}(q, f) \}$
- xvii. $C_{x^2-y^2}(q, f) = \frac{1}{\sqrt{2}} \{ Y_{2,-2}(q, f) + Y_{2,2}(q, f) \}$
- xviii. $C_{xy}(q, f) = \frac{i}{\sqrt{2}} \{ Y_{2,-2}(q, f) - Y_{2,2}(q, f) \}$

Appendix: C

Translational operator in the presence of magnetic field

Let us consider the Dirac Hamiltonian in the uniform magnetic field \mathbf{B} with periodic potential $V(\mathbf{r})$ as

$$H = c\boldsymbol{\alpha} \cdot \{\mathbf{P} + e\mathbf{A}(\mathbf{r})\} + \beta mc^2 + V(\mathbf{r}). \quad (\text{C1})$$

The usual translation operator is defined as $T(\mathbf{R}_n) = e^{-i\mathbf{R}_n \cdot \mathbf{p}/\hbar}$. Consider the following relation

$$T(\mathbf{R}_n)HT(\mathbf{R}_n)^\dagger f(\mathbf{r}) = T(\mathbf{R}_n)HT(-\mathbf{R}_n)f(\mathbf{r}),$$

where $f(\mathbf{r})$ is a bispinor function.

$$\begin{aligned} &= T(\mathbf{R}_n)H f(\mathbf{r} + \mathbf{R}_n) \\ &= T(\mathbf{R}_n)[c\boldsymbol{\alpha} \cdot \{\mathbf{P} + e\mathbf{A}(\mathbf{r})\} + \beta mc^2 + V(\mathbf{r})]f(\mathbf{r} + \mathbf{R}_n) \\ &= [c\boldsymbol{\alpha} \cdot \{\mathbf{P} + e\mathbf{A}(\mathbf{r} - \mathbf{R}_n)\} + \beta mc^2 + V(\mathbf{r} - \mathbf{R}_n)]f(\mathbf{r}), \\ &= [c\boldsymbol{\alpha} \cdot \{\mathbf{P} + e\mathbf{A}(\mathbf{r} - \mathbf{R}_n)\} + \beta mc^2 + V(\mathbf{r})]f(\mathbf{r}). \\ &= H f(\mathbf{r}) \end{aligned}$$

Finally, the translated Hamiltonian is given by

$$T(\mathbf{R}_n)HT(\mathbf{R}_n)^\dagger = H = [c\boldsymbol{\alpha} \cdot \{\mathbf{P} + e\mathbf{A}(\mathbf{r} - \mathbf{R}_n)\} + \beta mc^2 + V(\mathbf{r})]. \quad (\text{C2})$$

Comparing Eqs. (C1) and (C2), the difference between them is just the vector potential part. In the case of uniform magnetic field $\mathbf{A}(\mathbf{r}) = (0, Bx, 0)$ and $\mathbf{A}(\mathbf{r} - \mathbf{R}_n) = [0, B(x - R_{nx}), 0]$ yield the same magnetic field $\mathbf{B} = (0, 0, B)$ (i.e. $\mathbf{B} = B\mathbf{e}_z$) because $\nabla \times \mathbf{A}(\mathbf{r}) = \nabla \times \mathbf{A}(\mathbf{r} - \mathbf{R}_n) = (0, 0, B)$. This means that $\mathbf{A}(\mathbf{r})$ and $\mathbf{A}(\mathbf{r} - \mathbf{R}_n)$ are related with each other by gauge transformation as,

$$A(\mathbf{r} \square \mathbf{R}_n) = A(\mathbf{r}) + \nabla \square(\mathbf{r}, \mathbf{R}_n) \quad (\text{C3})$$

Let $\Psi(\mathbf{r})$ be the eigen function of H , Then

$$H\Psi(\mathbf{r}) = E\Psi(\mathbf{r}) \quad (\text{C4})$$

$$\left[c\alpha \cdot \{ \mathbf{P} + e\mathbf{A}(\mathbf{r}) \} + \beta mc^2 + V(\mathbf{r}) \right] \Psi(\mathbf{r}) = E\Psi(\mathbf{r}) \quad (\text{C5})$$

Acting $T(\mathbf{R}_n)$ on the both side of Eq. (C4) from LHS, we have

$$T(\mathbf{R}_n)H\Psi(\mathbf{r}) = ET(\mathbf{R}_n)\Psi(\mathbf{r}).$$

$$T(\mathbf{R}_n)HT(\mathbf{R}_n)^\dagger T(\mathbf{R}_n)\Psi(\mathbf{r}) = ET(\mathbf{R}_n)\Psi(\mathbf{r}) \quad (\text{C6})$$

$$HT(\mathbf{R}_n)\Psi(\mathbf{r}) = ET(\mathbf{R}_n)\Psi(\mathbf{r}). \quad (\text{C7})$$

Substituting Eq. (C2) into (C7), we have

$$\left[c\alpha \cdot \{ \mathbf{P} + e\mathbf{A}(\mathbf{r} - \mathbf{R}_n) \} + \beta mc^2 + V(\mathbf{r}) \right] T(\mathbf{R}_n)\Psi(\mathbf{r}) = ET(\mathbf{R}_n)\Psi(\mathbf{r}).$$

Using Eq. (C3), we have

$$\left[c\alpha \cdot \{ \mathbf{P} + e\mathbf{A}(\mathbf{r}) + e\nabla\chi(\mathbf{r}, \mathbf{R}_n) \} + \beta mc^2 + V(\mathbf{r}) \right] T(\mathbf{R}_n)\Psi(\mathbf{r}) = ET(\mathbf{R}_n)\Psi(\mathbf{r}) \quad (\text{C8})$$

Comparing Eqs. (C5) and (C8), we can say that $T(\mathbf{R}_n)\Psi(\mathbf{r})$ can be obtained from the gauge transformation of $\Psi(\mathbf{r})$. Namely

$$T(\mathbf{R}_n)\Psi(\mathbf{r}) = e^{-\frac{ie}{\hbar}\chi(\mathbf{r}, \mathbf{R}_n)} \Psi(\mathbf{r}) \quad (\text{C9})$$

Substituting Eq. (C9) into (C6), we have

$$T(\mathbf{R}_n)HT(\mathbf{R}_n)^\dagger e^{-\frac{ie}{\hbar}\chi(\mathbf{r}, \mathbf{R}_n)} \Psi(\mathbf{r}) = E e^{-\frac{ie}{\hbar}\chi(\mathbf{r}, \mathbf{R}_n)} \Psi(\mathbf{r})$$

Multiplying $\exp\{ie\chi(\mathbf{r}, \mathbf{R}_n)/\hbar\}$ on the both side, then

$$\left\{ e^{\frac{ie}{\hbar}\chi(\mathbf{r}, \mathbf{R}_n)} T(\mathbf{R}_n) \right\} H \left\{ e^{\frac{ie}{\hbar}\chi(\mathbf{r}, \mathbf{R}_n)} T(\mathbf{R}_n) \right\}^\dagger \Psi(\mathbf{r}) = E\Psi(\mathbf{r}) \quad (\text{C10})$$

Substituting Eq. (C4) into (C10), we have

$$\left\{ e^{\frac{ie}{\hbar}\chi(\mathbf{r}, \mathbf{R}_n)} T(\mathbf{R}_n) \right\} H \left\{ e^{\frac{ie}{\hbar}\chi(\mathbf{r}, \mathbf{R}_n)} T(\mathbf{R}_n) \right\}^\dagger \Psi(\mathbf{r}) = H\Psi(\mathbf{r})$$

$$\left\{ e^{\frac{i\epsilon}{\hbar}\chi(\mathbf{r}, \mathbf{R}_n)} T(\mathbf{R}_n) \right\} H \left\{ e^{\frac{i\epsilon}{\hbar}\chi(\mathbf{r}, \mathbf{R}_n)} T(\mathbf{R}_n) \right\}^\dagger = H$$

$$U(\mathbf{R}_n) H U(\mathbf{R}_n)^\dagger = H,$$

where

$$U(\mathbf{R}_n) = e^{\frac{i\epsilon}{\hbar}\chi(\mathbf{r}, \mathbf{R}_n)} T(\mathbf{R}_n) \quad (\text{C11})$$

is called the magnetic translation operator, the set of such operators commute with each other. Here $T(\mathbf{R}_n) = \exp(-i\mathbf{R}_n \cdot \mathbf{p} / \hbar)$ denotes the usual translation operator. It is easily shown that $U(\mathbf{R}_n)$ commutes with the Hamiltonian [Eq. (3.2)],

$$[H, U(\mathbf{R}_n)] = 0.$$

The multiplication of $U(\mathbf{R}_n)$ and $U(\mathbf{R}_m)$ leads to

$$\begin{aligned} U(\mathbf{R}_n)U(\mathbf{R}_m) &= e^{\frac{i\epsilon}{\hbar}\chi(\mathbf{r}, \mathbf{R}_n)} T(\mathbf{R}_n) e^{\frac{i\epsilon}{\hbar}\chi(\mathbf{r}, \mathbf{R}_m)} T(\mathbf{R}_m) \\ &= e^{\frac{i\epsilon}{\hbar}\chi(\mathbf{r}, \mathbf{R}_n)} T(\mathbf{R}_n) e^{\frac{i\epsilon}{\hbar}\chi(\mathbf{r}, \mathbf{R}_m)} T(\mathbf{R}_n)^\dagger T(\mathbf{R}_n) T(\mathbf{R}_m) \\ &= e^{\frac{i\epsilon}{\hbar}\chi(\mathbf{r}, \mathbf{R}_n)} e^{\frac{i\epsilon}{\hbar}\chi(\mathbf{r}-\mathbf{R}_n, \mathbf{R}_m)} T(\mathbf{R}_n) T(\mathbf{R}_m) \\ &= e^{\frac{i\epsilon}{\hbar}\chi(\mathbf{r}, \mathbf{R}_n)} e^{\frac{i\epsilon}{\hbar}\chi(\mathbf{r}-\mathbf{R}_n, \mathbf{R}_m)} T(\mathbf{R}_n + \mathbf{R}_m) \\ &= e^{\frac{i\epsilon}{\hbar}\chi\{(\mathbf{r}, \mathbf{R}_n) + \chi(\mathbf{r}-\mathbf{R}_n, \mathbf{R}_m)\}} e^{-\frac{i\epsilon}{\hbar}\chi(\mathbf{r}, \mathbf{R}_n + \mathbf{R}_m)} e^{\frac{i\epsilon}{\hbar}\chi(\mathbf{r}, \mathbf{R}_n + \mathbf{R}_m)} T(\mathbf{R}_n + \mathbf{R}_m) \\ &= e^{\frac{i\epsilon}{\hbar}\chi\{(\mathbf{r}, \mathbf{R}_n) + \chi(\mathbf{r}-\mathbf{R}_n, \mathbf{R}_m) - \chi(\mathbf{r}, \mathbf{R}_n + \mathbf{R}_m)\}} U(\mathbf{R}_n + \mathbf{R}_m) \end{aligned}$$

Using the relation $\chi(\mathbf{r}, \mathbf{R}_n) = -BR_{nx}y$, we have

$$U(\mathbf{R}_n)U(\mathbf{R}_m) = e^{\frac{i\epsilon}{\hbar}BR_{mx}R_{ny}} U(\mathbf{R}_n + \mathbf{R}_m). \quad (\text{C12})$$

The lattice vectors of the two dimensional square lattice with lattice constant is given by

$$\mathbf{R}_n = n_1 \mathbf{a}_x + n_2 \mathbf{a}_y \text{ or } \mathbf{R}_n = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 \quad (\text{C13})$$

Where n_1 and n_2 are integers, and $\mathbf{a}_1 = a\mathbf{e}_x$, $\mathbf{a}_2 = a\mathbf{e}_y$. The magnetic field is directed along the z-axis, and its magnitude B is given by

$$B = \frac{2\pi\hbar}{ea^2} \frac{p}{q}, \quad (\text{C14})$$

where p and q are relatively prime integers. In the same way, we can show that

$$U(\mathbf{R}_m)U(\mathbf{R}_n) = e^{i\frac{e}{\hbar}B\mathbf{R}_m \cdot \mathbf{R}_n} U(\mathbf{R}_m + \mathbf{R}_n). \quad (\text{C15})$$

From Eqs. (C12) and (C15), we have

$$\begin{aligned} U(\mathbf{R}_n)U(\mathbf{R}_m) &= e^{i\frac{e}{\hbar}B(\mathbf{R}_m \cdot \mathbf{R}_n - \mathbf{R}_n \cdot \mathbf{R}_m)} U(\mathbf{R}_m)U(\mathbf{R}_n) \\ U(\mathbf{R}_n)U(\mathbf{R}_m) &= e^{-2\pi i \frac{p}{q}(m_1 n_2 - n_1 m_2)} U(\mathbf{R}_m)U(\mathbf{R}_n). \end{aligned} \quad (\text{C16})$$

From this relation, if we take the set of the magnetic translation operators such as

$$\{U(\mathbf{t}_n) \mid \mathbf{t}_n = n_1 \mathbf{a}_1 + n_2 q \mathbf{a}_2\}, \quad (\text{C17})$$

then this set form an Abelian group [45]. Namely, we have

$$U(\mathbf{t}_n)U(\mathbf{t}_m) = U(\mathbf{t}_m)U(\mathbf{t}_n). \quad (\text{C18})$$

Note that the set of translation vector \mathbf{t}_n represents a two-dimensional rectangular lattice with a unit cell of sides a and aq (see, Fig. 4.1). In general, the eigen functions of the Hamiltonian, which belongs to a degenerate level, form basis functions of the irreducible representations (IRs) of the symmetry group of the Hamiltonian [46, 47]. In addition, all IRs of an Abelian group are necessarily one-dimensional [47]. Therefore, eigen functions $\Phi_k(\mathbf{r})$ are basis functions of IRs of the Abelian group Eq. (4.11), we have

$$U(\mathbf{t}_n)\Phi_k(\mathbf{r}) = C(\mathbf{t}_n)\Phi_k(\mathbf{r}), \quad (\text{C19})$$

where $C(\mathbf{t}_n)$ is the IR of the Abelian group.

Appendix: D

Derivation of magnetic Bloch theorem

From the magnetic translational operator $U(\mathbf{R}_n) = e^{i\frac{e}{\hbar}\chi(\mathbf{r}, \mathbf{R}_n)} T(\mathbf{R}_n)$, we can show that

$$U(\mathbf{R}_n)^\dagger H U(\mathbf{R}_n) = H. \quad (\text{D1})$$

This means that, this system is invariant under translation i.e. the system has translational symmetry. Eq. (D1) implies that

$$[H, U(\mathbf{R}_n)] = 0. \quad (\text{D2})$$

On the other hand, choose such set of translation vector $\{\mathbf{t}_n\}$ which are the subsets of $\{\mathbf{R}_n\}$ and satisfy the following relations

$$\begin{aligned} U(\mathbf{t}_n) U(\mathbf{t}_{n'}) &= U(\mathbf{t}_{n'}) U(\mathbf{t}_n), \\ [U(\mathbf{t}_n), U(\mathbf{t}_{n'})] &= 0. \end{aligned} \quad (\text{D3})$$

Equations (D2) and (D3) show that $H, U(\mathbf{t}_n), U(\mathbf{t}_{n'}), U(\mathbf{t}_{n''}) \dots$ are commute with each other. Therefore, we can say that $H, U(\mathbf{t}_n), U(\mathbf{t}_{n'}), U(\mathbf{t}_{n''}) \dots$ have the simultaneous eigen function. Let us denote the simultaneous eigen function be $\Phi(\mathbf{r})$ then

$$H \Phi(\mathbf{r}) = E \Phi(\mathbf{r}), \quad (\text{D4})$$

and

$$U(\mathbf{t}_n) \Phi(\mathbf{r}) = C(\mathbf{t}_n) \Phi(\mathbf{r}). \quad (\text{D5})$$

Operating $U(\mathbf{t}_n)$ on both side of Eq. (D4), we have

$$U(\mathbf{t}_n) H \Phi(\mathbf{r}) = E U(\mathbf{t}_n) \Phi(\mathbf{r}).$$

Using the relation $U(\mathbf{t}_n) H = H U(\mathbf{t}_n)$, then

$$H \{U(\mathbf{t}_n) \Phi(\mathbf{r})\} = E \{U(\mathbf{t}_n) \Phi(\mathbf{r})\}. \quad (\text{D6})$$

Equation (D6) shows that $\{U(\mathbf{t}_n)\Phi(\mathbf{r})\}$ is also an eigen function of H . Therefore, we can say that $\Phi(\mathbf{r})$ and $\{U(\mathbf{t}_n)\Phi(\mathbf{r})\}$ are related with each other by gauge transformation. According to normalization condition

$$\int |U(\mathbf{t}_n)\Phi(\mathbf{r})|^2 d^3r = 1. \quad (\text{D7})$$

Substituting Eq. (D5) into (D7), we have

$$\begin{aligned} \int |C(\mathbf{t}_n) \Phi(\mathbf{r})|^2 d^3r &= 1, \\ |C(\mathbf{t}_n)|^2 \int |\Phi(\mathbf{r})|^2 d^3r &= 1 \\ |C(\mathbf{t}_n)|^2 &= 1 \end{aligned} \quad (\text{D8})$$

where $\int |\Phi(\mathbf{r})|^2 d^3r = 1$. Thus from Eq. (D8), $C(\mathbf{t}_n) = e^{2\pi i k}$, k is a real number. Therefore, Eq. (D5) becomes

$$U(\mathbf{t}_n)\Phi(\mathbf{r}) = e^{2\pi i k} \Phi(\mathbf{r}) \quad (\text{D9})$$

Let us define translation vector $\mathbf{t}_n = n_1 a_x \mathbf{e}_x + n_2 a_y \mathbf{e}_y + n_3 a_z \mathbf{e}_z$ or $\mathbf{t}_n = n_1 \mathbf{a}_1 + n_2 q \mathbf{a}_2 + n_3 \mathbf{a}_3$, where \mathbf{a}_1 , \mathbf{a}_2 , and \mathbf{a}_3 are the primitive lattice vectors and n_1 , n_2 , and n_3 are integers, then Eq. (D9) can be written as

$$U(\mathbf{a}_1) \Phi(\mathbf{r}) = e^{2\pi i k_1} \Phi(\mathbf{r}), \quad (\text{D10})$$

$$U(\mathbf{a}_2) \Phi(\mathbf{r}) = e^{2\pi i k_2} \Phi(\mathbf{r}), \quad (\text{D11})$$

$$U(\mathbf{a}_3) \Phi(\mathbf{r}) = e^{2\pi i k_3} \Phi(\mathbf{r}), \quad (\text{D12})$$

where k_1 , k_2 and k_3 are real numbers. Again we have

$$U(n_1 \mathbf{a}_1) = U(\mathbf{a}_1) U(\mathbf{a}_1) \cdots \cdots U(\mathbf{a}_1) \quad (\text{D13})$$

$$U(n_2 q \mathbf{a}_2) = U(q \mathbf{a}_2) U(q \mathbf{a}_2) \cdots \cdots U(q \mathbf{a}_2) \quad (\text{D14})$$

$$U(n_3 \mathbf{a}_3) = U(\mathbf{a}_3) U(\mathbf{a}_3) \cdots \cdots U(\mathbf{a}_3) \quad (\text{D15})$$

then $U(\mathbf{t}_n) \Phi(\mathbf{r})$ can be written as

$$U(\mathbf{t}_n) \Phi(\mathbf{r}) = U(n_1 \mathbf{a}_1 + n_2 q \mathbf{a}_2 + n_3 \mathbf{a}_3) \Phi(\mathbf{r})$$

$$\begin{aligned}
&= U(n_1 \mathbf{a}_1) U(n_2 q \mathbf{a}_2) U(n_3 \mathbf{a}_3) \Phi(\mathbf{r}) \\
&= \underbrace{U(\mathbf{a}_1) \cdots U(\mathbf{a}_1)}_{n_1} \underbrace{U(q \mathbf{a}_2) \cdots U(q \mathbf{a}_2)}_{n_2} \underbrace{U(\mathbf{a}_3) \cdots U(\mathbf{a}_3)}_{n_3} \Phi(\mathbf{r})
\end{aligned} \tag{D16}$$

Substituting Eqs. (D10), (D11) and (D12) into (D16), we get

$$U(\mathbf{t}_n) \Phi(\mathbf{r}) = e^{2\pi i(n_1 k_1 + q n_2 k_2 + n_3 k_3)} \Phi(\mathbf{r}). \tag{D17}$$

The wave vector \mathbf{k} is defined as

$$\mathbf{k} = k_1 \mathbf{b}_1 + k_2 \mathbf{b}_2 + k_3 \mathbf{b}_3,$$

where \mathbf{b}_1 , \mathbf{b}_2 and \mathbf{b}_3 are the magnetic reciprocal lattice vectors defined as

$$\mathbf{b}_1 = 2\pi \frac{q \mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot (q \mathbf{a}_2 \times \mathbf{a}_3)}; \quad \mathbf{b}_2 = 2\pi \frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_1 \cdot (q \mathbf{a}_2 \times \mathbf{a}_3)}; \quad \mathbf{b}_3 = 2\pi \frac{\mathbf{a}_1 \times q \mathbf{a}_2}{\mathbf{a}_1 \cdot (q \mathbf{a}_2 \times \mathbf{a}_3)}.$$

Furthermore,

$$\mathbf{k} \cdot \mathbf{t}_n = 2\pi(k_1 n_1 + q k_2 n_2 + k_3 n_3).$$

Finally, Eq. (D17) becomes

$$U(\mathbf{t}_n) \Phi(\mathbf{r}) = e^{i \mathbf{k} \cdot \mathbf{t}_n} \Phi(\mathbf{r}). \tag{D18}$$

In addition, we have

$$\begin{aligned}
U(\mathbf{t}_n) \Phi(\mathbf{r}) &= e^{\frac{i e}{\hbar} \chi(\mathbf{r}, \mathbf{t}_n)} T(\mathbf{t}_n) \Phi(\mathbf{r}) \\
&= e^{\frac{i e}{\hbar} \chi(\mathbf{r}, \mathbf{t}_n)} \Phi(\mathbf{r} - \mathbf{t}_n)
\end{aligned} \tag{D19}$$

Comparing Eqs. (D18) and (D19), we have

$$\Phi(\mathbf{r} - \mathbf{t}_n) = e^{-\frac{i e}{\hbar} \chi(\mathbf{r}, \mathbf{t}_n)} e^{i \mathbf{k} \cdot \mathbf{t}_n} \Phi(\mathbf{r}) \tag{D20}$$

Equation (D20) 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. Equation (D20) is called magnetic Bloch theorem and is reduced to usual Bloch theorem when $B = 0$.

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