APPLICATION OF QKKR METHOD TO COMPLEX CRYSTALS

YANG WANG

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by

Yang Wang

A Thesis Submitted to the Faculty of the
College of Science
in Partial Fulfillment of the Requirements for
the Degree of Master of Science

Florida Atlantic University
Boca Raton,Florida
August 1989

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This thesis was prepared under the direction of the candidate's advisor, Dr. J. Samuel Faulkner, Department of Physics, and has been approved by the members of the supervisory committee. It was submitted to the faculty of the College of Science and was accepted in partial fulfillment of the requirements for the degree of Master of Science in Physics.

SUPERVISORY COMMITTEE:

J S Faulkner
(Thesis Advisor)

R F Stetson

Joseph R. Go

Chairman, Department
of Physics

Dean, College of Science

Dean of Graduate Studies

6/22/87
Date

ACKNOWLEDGMENTS

I would like to thank Dr. J. Samuel Faulkner for his advice and encouragement during my research and the preparation of this thesis. I have benefitted greatly from Dr. Antonis Andriotis and our very helpful discussions, and from Dr. Don M. Nicholson for his providing me many useful programs.

I would also like to thank Ms. Carol S. Schwob for her permission to use the laser printer in the Academic Computing Center.

Yang Wang

ABSTRACT

Author:	Yang Wang
Title:	Application of QKKR method to Complex Crystals.
Institution:	Florida Atlantic University
Degree:	Master of Science in Physics
Year:	1989

The QKKR method is a recently invented band theory with remarkable advantages of fast computational speed and no special requirements on the one electron potential. It has been successfully applied to the band structure calculation for simple crystals. A program for QKKR band theory calculations for complex crystals (more than one atom per unit cell) is developed and applied to PdH. It is shown that, compared with the KKR method, the QKKR method is more efficient and yields very accurate results in the range of energies in which we are interested. Unlike other band theories, the QKKR requires the expansion of a three dimensional step function in real spherical harmonics. A general method for evaluating this expansion is established in this thesis.

CONTENTS

LIST OF FIGURES

CHAPTER 1

INTRODUCTION

1.1 OUTLINE OF THESIS

Since the KKR method (also called the Green's function method) was first developed by Korringa[1], Kohn and Rostoker[2], it has been proved that this is one of the most successful band theory methods because of its ability to yield quantitatively accurate results and rapid convergence[3]. However, a lot of efforts have been made by some scientists to improve the technique of the calculation and eliminate the requirement of a special shape for the one-electron potential[4,5,6,7]. The most remarkable progress on this aspect must be due to the QKKR method, proposed by Dr. Faulkner[8] in 1982.

Derived from the multiple-scattering theory, the QKKR method gives a new band theory equation for calculating the one-electron energy eigenvalues and wave functions. The most important advantage of the QKKR method is that, instead of looking for every zero of the determinant of the KKR secular equation matrix relating to a certain vector **k**, it finds all of the eigenvalues for each vector **k** by diagonalizing a single matrix. Compared with the KKR method, it saves a large amount of computing time without losing accuracy over the range of energy bands of interest.

The band structure calculations for both simple crystals with one atom per unit cell, e.g. Cu, Zn, Na,... etc, and complex crystals, which have more than one atom per unit cell, e.g. Si, NaCl, GaAs, PdH... etc, have been carried out in KKR method by a lot of people[9,10,11,12]. Previously the QKKR method has been applied only to the band structure calculations for simple crystals[8,13]. In order to develop a complete QKKR method that could replace the KKR method and be used for wide range of purposes, especially for alloy theory in the future, it is necessary to study its application to the band theory for complex crystals and develop the necessary computer programs. This is the purpose of this thesis. The sample material considered in my research is PdH, which has been widely studied by many people using various methods[14,15,16,17].

In the second chapter, I will briefly review the multiple-scattering theory. Then both KKR and QKKR methods will be derived based on this theory in chapter 3 and chapter 4, respectively. In these two chapters, the formulas for both simple and complex lattice structures are provided.

In QKKR theory, the three dimensional step function $\sigma(\mathbf{r})$, which equals 1 inside and zero outside a polyhedron, plays a very important role. A general method for evaluating the expansion of $\sigma(\mathbf{r})$ in terms of real spherical functions $Y_L(\mathbf{r})$, defined in Appendix II, is invented and discussed thoroughly in chapter 5.

Chapter 6 gives the detailed discussion of the procedures and techniques in applying both KKR and QKKR methods to the band structure calculation for the complex crystal PdH. The E vs. **k** curves derived from the both methods are provided and compared to each other to demonstrate how successful the QKKR method is in the case of complex crystals. The conclusions of my work and results are put in the last chapter.

Before turning to the derivations of KKR and QKKR theory, it is helpful to consider some basic concepts.

1.2 CRYSTAL STRUCTURE

It is well-known that a perfect crystal can be represented by a set of periodic lattice points with a certain basis of atoms, say N atoms, around each point. The position of each atom in the basis relative to the associated lattice point is denoted as a vector $\mathbf{q}_i$, $i=1,2,\cdots N$. Conventionally, the coordinate system is set in such a way that the origin is at a lattice point, which we call the central lattice point, and the position vector of nth lattice point is denoted as $\mathbf{R}_n$.

According to the one-electron approximation, the one electron wave functions $\Psi_{\mathbf{k}}^{\lambda}(\mathbf{r})$ will satisfy the following single particle Schrödinger equation (assuming atomic units, see Appendix I.)

$$[\ -\nabla^2 + V(\mathbf{r})\ ]\cdot\Psi_{\mathbf{k}}^{\lambda}(\mathbf{r}) = E^{\lambda}(\mathbf{k})\Psi_{\mathbf{k}}^{\lambda}(\mathbf{r}) \quad , \tag{1.1}$$

where $\mathbf{k}$ is a vector in reciprocal lattice space, λ refers to the index of a certain band and $V(\mathbf{r})$ is the one electron potential. In a perfect crystal, $V(\mathbf{r})$ must have the periodicity of the crystal and can be written as

$$V(\mathbf{r} + \mathbf{R}_n) = V(\mathbf{r}) \ . \tag{1.2}$$

The Bloch theorem states that the one-electron wave function (also called Bloch wave function) associated with energy E satisfies

$$\Psi_{\mathbf{k}}^{\lambda}(\mathbf{r} + \mathbf{R}) = e^{i\mathbf{k}\cdot\mathbf{R}n} \cdot \Psi_{\mathbf{k}}^{\lambda}(\mathbf{r}) \ . \tag{1.3}$$

Assuming that the one-electron potential is composed of a set of local and non-overlapping potentials, we have

$$V(\mathbf{r}) = \begin{cases} v_i(\mathbf{r} - \mathbf{R}_n - \mathbf{q}_i) & r \in \Omega_n(i) \\ V_0 & r \in \text{interstitial area} \ , \end{cases} \tag{1.4}$$

where $v_i(\mathbf{r} - \mathbf{R}_n - \mathbf{q}_i)$ is the local potential defined in the region $\Omega_n(i)$ and due to the atom locating at the position $\mathbf{q}_i$ relative to nth lattice point, and V_0 is a constant potential within the interstitial area between the regions $\Omega_n(i)$.

From the equation (1.1), it is obvious that the constant interstitial potential can be set to zero by subtracting the energy with V_0. Usually we will assume that the interstitial potential is zero unless giving a special statement. Therefore, the one-electron potential can be written as

$$V(\mathbf{r}) = \sum_{n,i} v_i(\mathbf{r} - \mathbf{R}_n - \mathbf{q}_i) \ . \tag{1.5}$$

If the potentials $v_i(\mathbf{r} - \mathbf{R}_n - \mathbf{q}_i)$ are spherically symmetric with $R_{mt}(i)$ being the radius of the spherical region $\Omega_n(i)$, i.e.

$$v_i(\mathbf{r} - \mathbf{R}_n - \mathbf{q}_i) = v_i(|\mathbf{r} - \mathbf{R}_n - \mathbf{q}_i|) \qquad (1.6)$$

$$\text{for } |\mathbf{r} - \mathbf{R}_n - \mathbf{q}_i| \leq R_{mt}(i) \ ,$$

the one-electron potential $V(\mathbf{r})$ is called a muffin-tin potential and the radii $R_{mt}(i)$ are muffin-tin radii.

1.3 UNIT CELL

Usually it is useful to construct a lattice cell that contains one or more lattice points and will fill all the space through the action of suitable displacements with vectors $\mathbf{R}_n$ so that the lattice space is composed of identical lattice cells. A unit cell is defined as the lattice cell inside which there is only one lattice point. The simple crystal is one whose lattice unit cell contains one atom, and a complex crystal has more than one atom in the unit cell. The central unit cell refers to the one containing the central lattice point.

Although there is more than one method to construct a unit cell, the Wigner-Seitz cell is the most useful. Its boundaries are composed of planes which are perpendicular to and intersecting at the mid-point of a line connecting the inside lattice point and one of its neighboring lattice points. As an example, the metal Cu has so-called FCC (face-centered cubic) lattice structure (see Fig.1-1), and its Wigner-Seitz cell is a regular rhombic dodecahedron (see Fig.1-2).

In this thesis, I choose the Wigner-Seitz cell as a unit cell for simple crystal structures. For complex crystals, the unit cell is divided into sub-cells, each of which contains one atom. They are constructed to contain the muffin-tin sphere of each atom in the unit cell. An example of this case is NaCl (see Fig.1-3), which lattice structure is FCC and unit cell is constructed in the way shown in Fig.1-4.

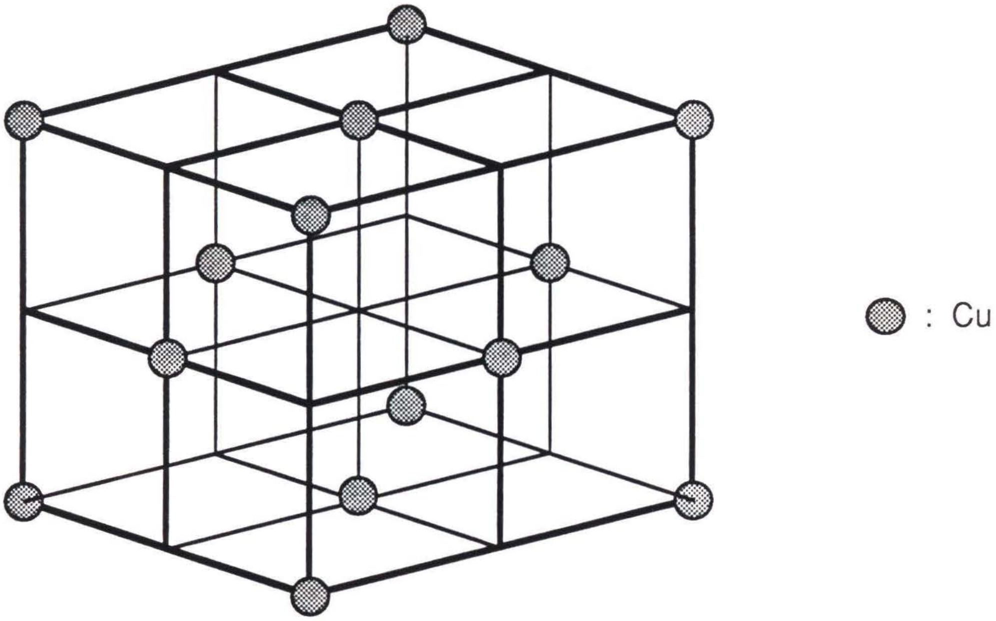

Fig. 1-1. The crystal structure of Cu is FCC type. There is one atom per unit cell.

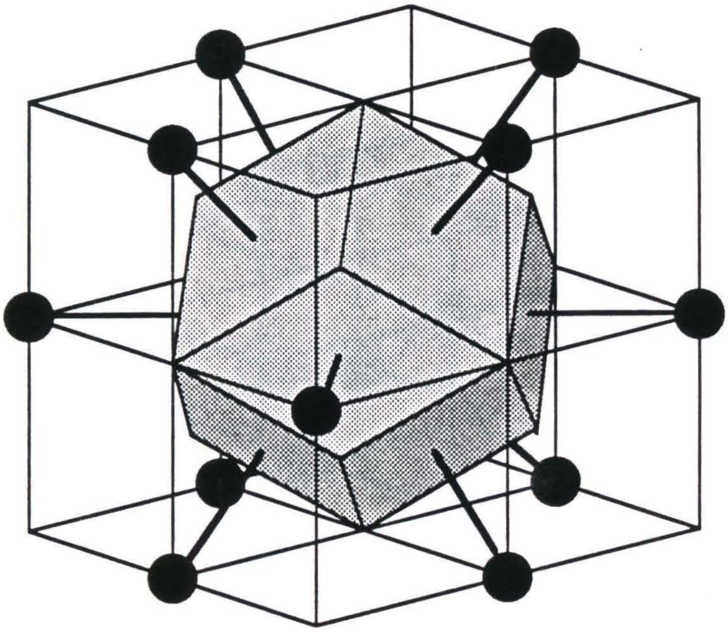

Fig. 1-2. The shadowed area is the Wigner-Seitz cell of FCC lattice structure.

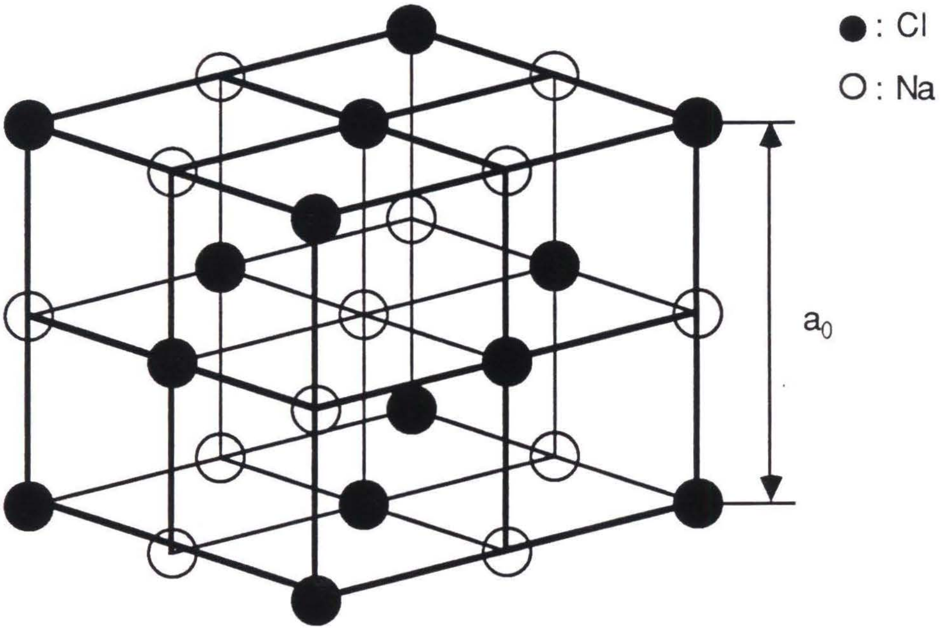

Fig. 1-3. The crystal structure of NaCl is FCC type. There are two atoms per unit cell.

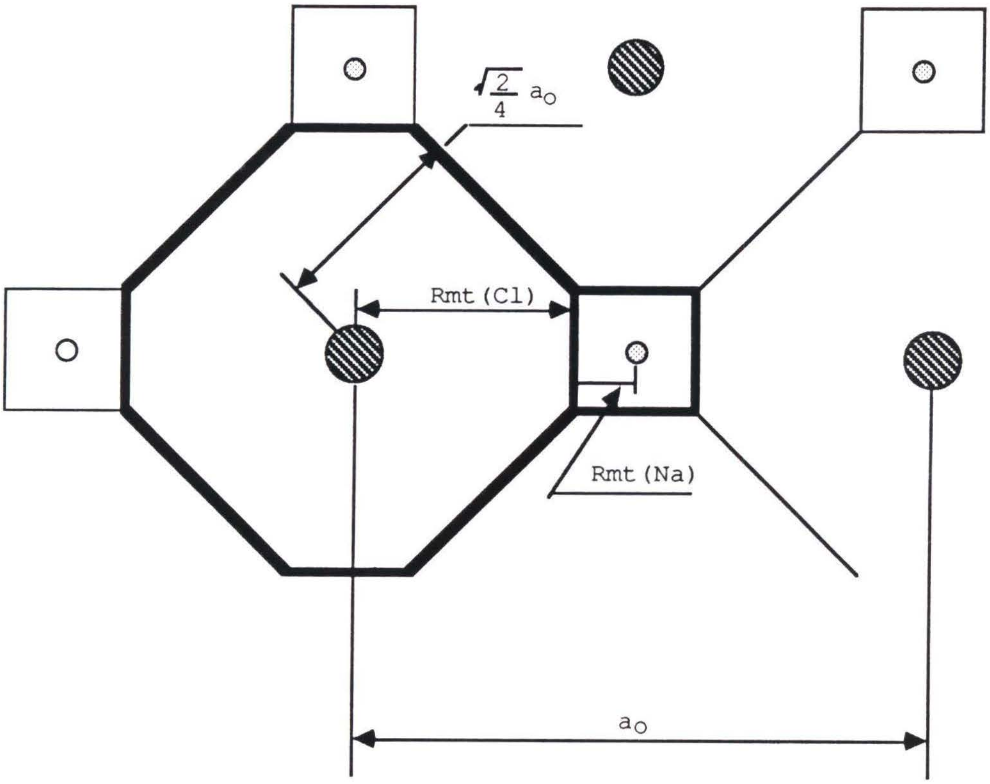

Fig. 1-4. The area bounded by the bold lines is the unit cell of NaCl lattice. The unit cell is divided into two sub-cells, each of which contains one atom, Na or Cl.

CHAPTER 2

MULTIPLE-SCATTERING THEORY

2.1 INTRODUCTION

Multiple scattering theory deals with a particle that is scattered by the potential V composed of a collection of local and non-overlaping potentials v_n, i.e.

$$V = \sum_n v_n \ . \tag{2.1}$$

The first contributions to this theory were in the late nineteenth century. Rayleigh[18], Ewald[19] and Kasterin[20] were the persons who made the major early developments of this theory. In the following section, a brief review of this theory is given within the frame work of formal scattering. More information about multiple scattering theory and its application to solid state physics can be found in Faulkner's book[21].

2.2 MULTIPLE SCATTERING THEORY

Usually in formal scattering theory the first step is to write the Lipmann-Schwinger equation[22]

$$|\Psi> = |\chi> + G_0 V|\Psi> , \tag{2.2}$$

where the potential V is described by (4.1), $|\chi>$ satisfies the unperturbed Schrödinger equation

$$H_0|\chi> = E|\chi> , \tag{2.3}$$

and $|\Psi>$, the state vector of the single particle, is the solution of Schrödinger's equation

$$(H_0 + V)|\Psi> = E|\Psi> , \tag{2.4}$$

corresponding to the same energy E in (4.3). The operator G_0 is defined as

$$G_0 = \lim_{\epsilon \to 0} (E + i\epsilon - H_0)^{-1} \quad . \tag{2.5}$$

By introducing the well-known transition-matrix T, which is related to the transition probability and defined as

$$T|\chi> = V|\Psi> , \tag{2.6}$$

we can rewrite the Lipmann-Schwinger equation as following

$$|\Psi> = |\chi> + G_0 T|\chi> \ . \qquad (2.7)$$

The T-matrix may be written in the form as

$$T = V\cdot(1 + G_0 T) \ , \qquad (2.8)$$

which can be shown to be equivalent to (2.6).

The basic idea of the multiple scattering theory is to obtain the T-matrix describing the scattering of a system of many scatterers in terms of the corresponding t-matrix for individual scatterers. This is accomplished by considering (2.1) and introducing

$$Q_n = v_n\cdot(1 + G_0 T) \ , \qquad (2.9)$$

so that

$$T = \sum_n Q_n \ . \qquad (2.10)$$

According to (2.8), the t matrix for scattering from the nth scatterer with potential v_n can be written as

$$t_n = v_n\cdot(1 + G_0 t_n) \ . \qquad (2.11)$$

Substituting T in (2.9) with (2.10), we can find

$$Q_n = v_n \cdot (1 + G_0 \cdot \sum_n Q_n) \quad , \tag{2.12}$$

or

$$\begin{aligned} Q_n &= (1 - v_n \cdot G_0)^{-1} v_n \cdot (1 + G_0 \cdot \sum_{m \neq n} Q_m) \\ &= t_n \cdot (1 + G_0 \cdot \sum_{m \neq n} Q_m) \quad . \end{aligned} \tag{2.13}$$

Obviously the T matrix for the system without nth scatterer will be $\sum_{m \neq n} Qm$. Therefore, comparing with (2.7),

$$|\Psi_n^i\rangle = |\chi\rangle + G_0 \cdot \sum_{m \neq n} Q_m |\chi\rangle \quad , \tag{2.14}$$

defines the incoming wave, scattered by other scatterers, to the nth scatterer. Because of (2.13), we have

$$t_n |\Psi_n^i\rangle = Q_n |\chi\rangle \quad , \tag{2.15}$$

$$\begin{aligned} |\Psi_n^i\rangle &= |\chi\rangle + G_0 \cdot \sum_{m \neq n} Q_m |\chi\rangle \\ &= |\chi\rangle + \sum_{m \neq n} G_0 \cdot t_m |\Psi_m^i\rangle \quad , \end{aligned} \tag{2.16}$$

and

$$|\Psi\rangle = |\chi\rangle + \sum_m G_0 \cdot t_m |\Psi_m^i\rangle \ . \qquad (2.17)$$

Equations (2.16) and (2.17) are called the fundamental equations of multiple scattering theory.

Notice that in solids the one-electron wave function $|\Psi\rangle$ is a stationary state, in which case T must be singular at the eigenvalues E. Therefore, in order to find nontrivial solution of the equation (2.7) for stationary state, we should set

$$|\chi\rangle = 0 \ . \qquad (2.18)$$

If we define the outgoing wave from nth scatterer as

$$|\Psi_n^o\rangle = G_0 \cdot t_n |\Psi_n^i\rangle \ , \qquad (2.19)$$

then (2.17) with the condition (2.18) gives

$$|\Psi\rangle = \sum_n |\Psi_n^o\rangle \ . \qquad (2.20)$$

This equation states that the total solution is the sum of the outgoing waves from all of the scatterers, or

$$|\Psi> = |\Psi_n^i> + |\Psi_n^o> , \qquad (2.21)$$

the solution is the sum of incoming and outgoing waves associated with any scatterer.

Notice that combining (2.17) and (2.18) with (2.19), we can find the incoming wave on any scatterer is the sum of outgoing waves from all other scatterers

$$|\Psi_n^i> = \sum_{m \neq n} |\Psi_m^o> . \qquad (2.22)$$

These last two equations, (2.21) and (2.22) are very important in the derivation of KKR theory.

CHAPTER 3

KKR THEORY

3.1 INTRODUCTION

There are two ways to derive the KKR method. One way was proposed in 1947 by Korringa from the point view of multiple scattering theory[1]. Another one was suggested in 1954 by Kohn and Rostoker through the variational principle method[2]. Many people[3,12] prefer the variational approach because of its simplicity in mathematical technique, but the derivation with multiple scattering theory provides a very clear physical picture and leads to some further developments[5,7] such as the invention of the QKKR method[8].

In this chapter, I will give a brief derivation of the KKR method using the results from the multiple scattering theory. A comprehensive discussion about this approach can be found in the paper[7] by Faulkner.

3.2 KKR THEORY

In last chapter, the multiple scattering theory has been discussed. We will find that it is a very powerful tool to solve the one-electron Schrödinger equation, which is the fundamental equation in band theory:

$$[-\nabla^2 + V(\mathbf{r})]\Psi^{\lambda}_{\mathbf{k}}(\mathbf{r}) = E^{\lambda}(\mathbf{k})\cdot\Psi^{\lambda}_{\mathbf{k}}(\mathbf{r}) \quad , \tag{3.1}$$

where the atomic units have been assumed (see Appendix I).

For simple crystals (the generalization to complex crystals is straightforward and will be considered in the section 3.3), the one-electron potential $V(\mathbf{r})$ is composed of a set of identical local non-overlapping potentials, $v(\mathbf{r} - \mathbf{R}_n)$, centered at the lattice points and can be written as

$$V(\mathbf{r}) = \sum_n v(\mathbf{r} - \mathbf{R}_n) \tag{3.2}$$

$$= \begin{cases} v(\mathbf{r} - \mathbf{R}_n) & \mathbf{r} \in \Omega_n \\ 0 & r \in \text{interstitial region} \ , \end{cases}$$

where Ω_n is the region centered at the nth lattice point with the local potential $v(\mathbf{r} - \mathbf{R}_n)$ being defined inside it.

To find the outgoing and incoming waves related to the nth scatterer, the intuitive approach is to look at the interstitial area outside the bounding sphere of Ω (see Fig.3-1 and Fig.3-2) where $V(\mathbf{r}) = 0$, and the wave function satisfies the Helmholtz equation

$$(-\nabla^2 - E)\cdot\phi(E,\mathbf{r}) = 0 \; . \tag{3.3}$$

We define $\mathbf{r}_n = \mathbf{r} - \mathbf{R}_n$ and $r_n = |\mathbf{r} - \mathbf{R}_n|$. Since the outgoing wave $\overset{o}{\phi}_n(E,\mathbf{r}_n)$ must be singular and the incoming wave $\overset{i}{\phi}_n(E,\mathbf{r}_n)$ must be regular as $r_n \longrightarrow 0$, we can expand $\overset{o}{\phi}_n(E,\mathbf{r}_n)$ in terms of $Y_L(\mathbf{r}_n)\cdot n_\ell(\alpha r_n)$ and $\overset{i}{\phi}_n(E,\mathbf{r}_n)$ in terms of $Y_L(\mathbf{r}_n)\cdot j_\ell(\alpha r_n)$ as follows

$$\overset{o}{\phi}_n(E,\mathbf{r}_n) = \alpha\cdot\sum_L Y_L(\mathbf{r}_n) n_\ell(\alpha r_n)\cdot\overset{n}{\xi}_L \qquad r \geq S \tag{3.4a}$$

$$\overset{i}{\phi}_n(E,\mathbf{r}_n) = \sum_L Y_L(\mathbf{r}_n) j_\ell(\alpha r_n)\cdot\overset{n}{\eta}_L \qquad r \geq S \tag{3.4b}$$

by defining

$$\alpha = \sqrt{E} \quad , \tag{3.5}$$

and S being the radius of the bounding sphere. For the area inside the sphere, let us assume $\alpha N_L(E,\mathbf{r}_n)$ and $J_L(E,\mathbf{r}_n)$ are the extensions of outgoing and incoming wave components with angular momentum L, respectively. Therefore, for $\mathbf{r}$

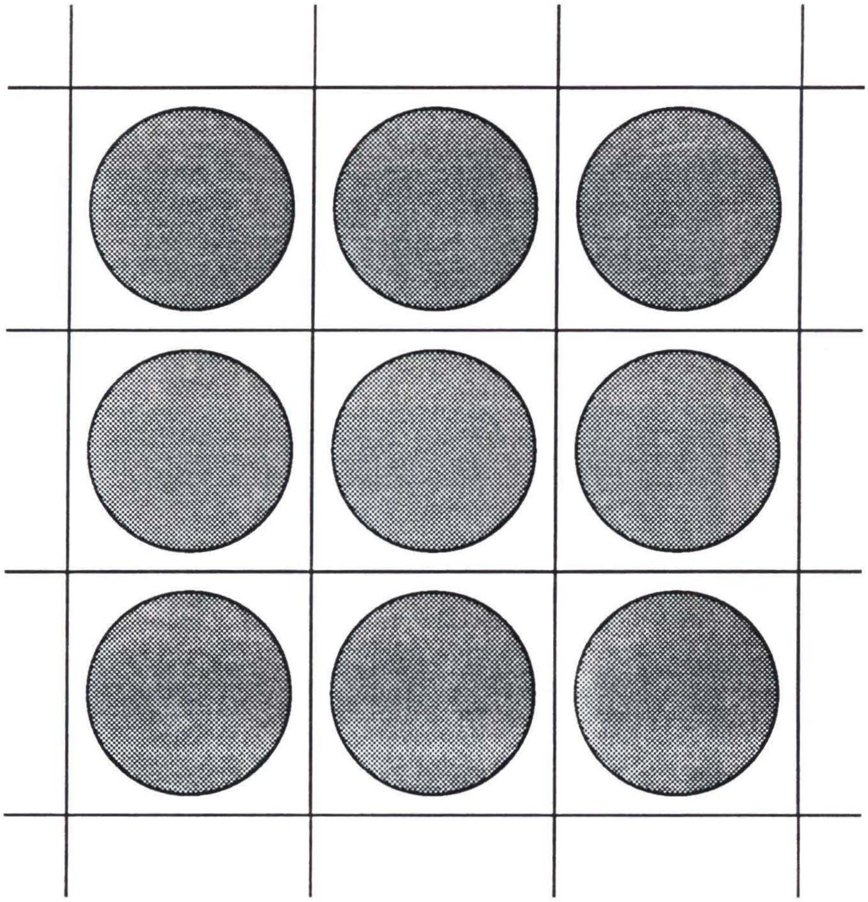

Fig. 3-1 An example of muffin-tin potential. The bounding spheres of local potentials do not overlap each other.

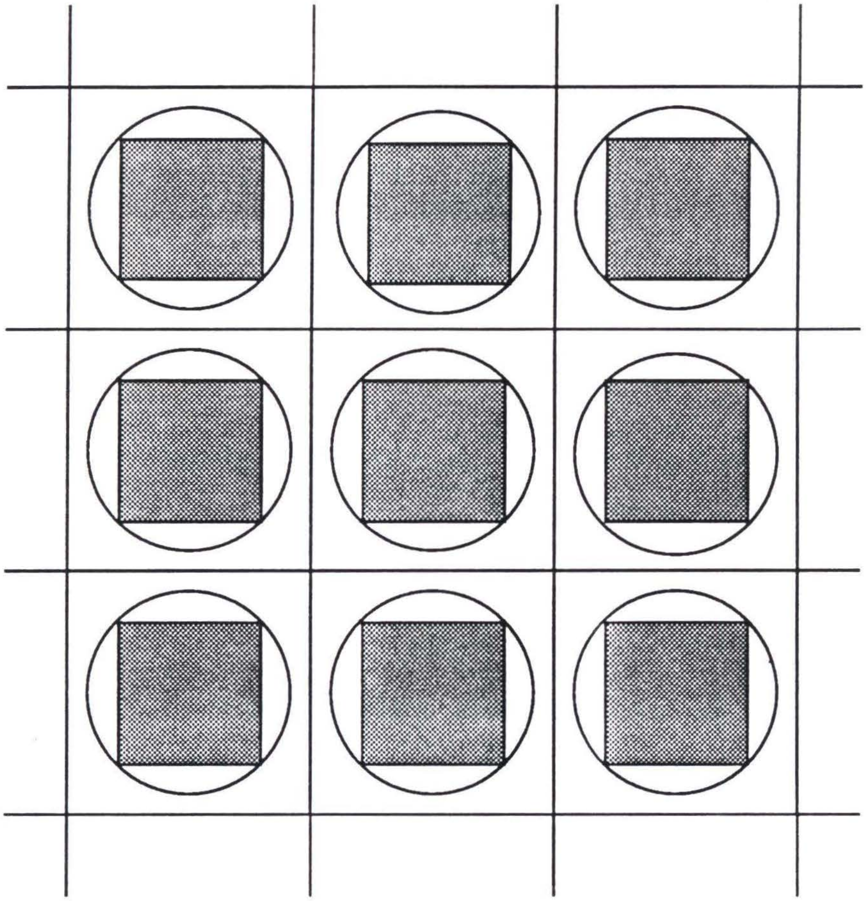

Fig. 3-2. An example of nonmuffin-tin potential. The bounding spheres of local potentials do not overlap each other.

either inside or outside the bounding sphere we have

$$\overset{o}{\phi}_n(E,\mathbf{r}_n) = \alpha\cdot\sum_L N_L(E,\mathbf{r}_n)\cdot\xi_L^n \,, \tag{3.6a}$$

$$\overset{i}{\phi}_n(E,\mathbf{r}_n) = \sum_L J_L(E,\mathbf{r}_n)\cdot\eta_L^n \,, \tag{3.6b}$$

with the conditions

$$\alpha N_L(E,\mathbf{r}_n) = \alpha Y_L(\mathbf{r}_n)\cdot n_\ell(\alpha\mathbf{r}_n) \qquad \text{if } r_n \geq S \tag{3.7a}$$

$$J_L(E,\mathbf{r}_n) = Y_L(\mathbf{r}_n)\cdot j_\ell(\alpha\mathbf{r}_n) \qquad \text{if } r_n \geq S \,. \tag{3.7b}$$

It can be shown[7] by considering the scattering of an incoming wave into an outgoing wave by the local potential that

$$\eta_L^n = -\sum_{L'} X_{LL'}(E)\cdot\xi_{L'}^n \,, \tag{3.8}$$

with

$$X_{LL'}(E) = \alpha\cdot\sum_{L''} C_{LL''}(E)\cdot S^{-1}_{L''L'}(E) \,. \tag{3.9}$$

The cosine and sine matrices in the equation (3.9) are

$$C_{LL'} = \alpha\cdot\int_{r\leq S} n_\ell(\alpha r) Y_L(\mathbf{r}) v(\mathbf{r})\phi_{L'}(E,\mathbf{r})\, d^3\mathbf{r} - \delta_{LL'} \tag{3.10a}$$

$$S_{LL'} = \alpha \cdot \int_{r \le S} j_\ell(\alpha r) Y_L(\mathbf{r}) v(\mathbf{r}) \phi_{L'}(E,\mathbf{r}) d^3\mathbf{r} \quad , \tag{3.10b}$$

where $\phi_{L'}(E,\mathbf{r})$ is the wave function component with angular momentum L′ and satisfies

$$(-\nabla^2 + v(\mathbf{r}) - E) \cdot \phi_{L'}(E,\mathbf{r}) = 0 \ , \tag{3.11a}$$

or

$$\phi_{L'}(E,\mathbf{r}) = Y_{L'}(\mathbf{r}) j_{\ell'}(\alpha r) - \int G(E,\mathbf{r},\mathbf{r}') v(\mathbf{r}') \times \phi_{L'}(E,\mathbf{r}') d^3\mathbf{r}', \tag{3.11b}$$

with

$$G(E,\mathbf{r},\mathbf{r}') = -\alpha \cdot \sum_L Y_L(\mathbf{r}) \cdot [j_\ell(\alpha r) n_\ell(\alpha r') - n_\ell(\alpha r) j_\ell(\alpha r')] \cdot Y_L(\mathbf{r}') . \tag{3.11c}$$

Thus the incoming wave can be written as

$$\overset{i}{\phi}_n(E,\mathbf{r}_n) = - \sum_{L,L'} J_L(E,\mathbf{r}_n) \cdot X_{LL'}(E) \cdot \xi^n_{L'} \ . \tag{3.12}$$

According to equation (2.21) in multiple scattering theory, we have

$$-\sum_{L,L'} J_L(E,\mathbf{r})\cdot X_{LL'}\cdot\xi_{L'} = \alpha\cdot\sum_{n\neq 0}\sum_{L'} N_L(E,\mathbf{r}_n)\cdot\xi^n_{L'} \ , \qquad (3.13)$$

where the subscript and superscript for n=0 on the left hand side of above equation are dropped off. Notice that the Bloch's theorem requires

$$\xi^n_L = e^{i\mathbf{k}\cdot\mathbf{R}n}\cdot\xi_L \ , \qquad (3.14)$$

so that eq. (3.13) becomes

$$\sum_{L'}\Big[\sum_L J_L(E,\mathbf{r})\cdot X_{LL'}(E) + \alpha\cdot\sum_{n\neq 0} N_{L'}(E,\mathbf{r}_n)\cdot e^{i\mathbf{k}\cdot\mathbf{R}n}\Big]\cdot\xi_{L'} = 0 \ . \qquad (3.15)$$

We can expand the outgoing waves from all other unit cells ($n \neq 0$) in terms of the incoming wave into the central unit cell ($n = 0$) as following, since $N_{L'}(E,\mathbf{r}_n)$ with $n \neq 0$ are regular within the central unit cell

$$\alpha\cdot N_L(E,\mathbf{r}_n) = \sum_{L'} J_{L'}(E,\mathbf{r})\cdot A^n_{LL'}(E) \ , \qquad (3.16)$$

with $\mathbf{r}$ being inside the central unit cell. Actually, the expansion coefficients $A^n_{LL'}$ can be found by considering the interstitial area inside the central unit cell but outside the bounding sphere of the region Ω

$$\alpha \cdot Y_L(\mathbf{r}_n) n_\ell(\alpha r_n) = \sum_{L'} Y_{L'}(\mathbf{r}) j_\ell(\alpha r) \cdot B^n_{LL'}(E) \quad , \tag{3.17}$$

so that

$$A^n_{LL'}(E) = B^n_{LL'}(E) \quad , \tag{3.18}$$

except for those n's which, in the case shown in Fig.3-3, are nearest neighboring unit cells with the bounding spheres of Ω_n overlapping with the one in the central unit cell. Define $N^n_{LL'}$ as the difference between $A^n_{LL'}$ and $B^n_{LL'}$ for those neighboring unit cells, so that

$$\begin{aligned} A_{LL'}(E,\mathbf{k}) &= \sum_{n\neq 0} e^{i\mathbf{k}\cdot\mathbf{R}n} . A^n_{LL'}(E) \\ &= B_{LL'}(E,\mathbf{k}) + N_{LL'}(E,\mathbf{k}) \quad , \end{aligned} \tag{3.19}$$

where $N_{LL'}(E,\mathbf{k})$ are called near-field corrections due to the overlapping effect mentioned above, and $B_{LL'}(E,\mathbf{k})$ are called structure constants

$$B_{LL'}(E,\mathbf{k}) = \sum_{n\neq 0} e^{i\mathbf{k}\cdot\mathbf{R}n} . B^n_{LL'}(E) \quad , \tag{3.20}$$

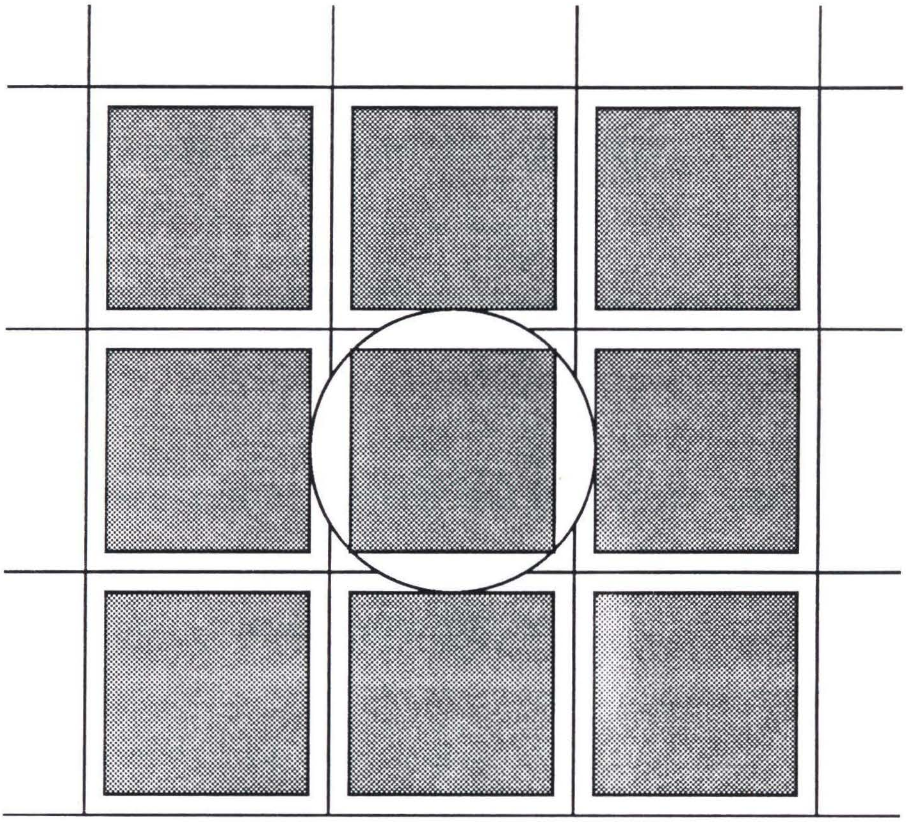

Fig. 3-3. An example of nonmuffin-tin potential. The bounding spheres of local potentials overlap each other.

which only depend on E, the **k** vector and the lattice structure. The technique of calculating structure constants was first treated by Ewald[19]. The explicit expression of these coefficients is available[3].

Therefore, combining (3.15) with (3.16) and (3.19), we have a set of homogeneous equations for $\xi_{L'}$

$$\sum_{L'} [\ X_{LL'}(E) + B_{LL'}(E,\mathbf{k}) + N_{LL'}(E,\mathbf{k})\ ]\cdot\xi_{L'} = 0\ . \tag{3.21}$$

In fact, the near-field corrections $N_{LL'}(E,\mathbf{k})$ can be ignored in practical calculations of interest, so that the nontrivial solutions of $\xi_{L'}$ exit only if

$$\det [\ \underline{X}(E) + \underline{B}(E,\mathbf{k})\ ] = 0\ , \tag{3.22}$$

which is the fundamental KKR equation for general potential. Thus, the E vs. **k** curves can be evaluated by looking for the energy eigenvalues E which satisfy the equation (3.22) for certain **k** vectors, and the Bloch waves are, according to (2.20)

$$\begin{aligned}\Psi^{\lambda}_{\mathbf{k}}(\mathbf{r}) &= \phi^{i}(E,\mathbf{r}) + \phi^{o}(E,\mathbf{r}) \\ &= \sum_{L} [\ \alpha\cdot N_{L}(E,\mathbf{r}) - \sum_{L'} J_{L'}(E,\mathbf{r})\cdot X_{LL'}(E)\ ]\cdot\xi^{\lambda}_{L}(\mathbf{k})\end{aligned}$$

$$= \sum_{L} Z_L(E^{\lambda}(\mathbf{k}),\mathbf{r})\cdot\xi^{\lambda}_{L}(\mathbf{k}) \quad , \tag{3.23}$$

with $\mathbf{r}$ inside the central unit cell and $Z_L(E^{\lambda}(\mathbf{k}),\mathbf{r})$ is a solution of the differential equation

$$[-\nabla^2 + v(\mathbf{r})]\cdot f(E,\mathbf{r}) = E\cdot f(E,\mathbf{r}) \quad , \tag{3.24}$$

with the boundary condition

$$Z_L(E,\mathbf{r}) = \alpha\cdot Y_L(\mathbf{r}) n_\ell(\alpha r) - \sum_{L'} Y_{L'}(\mathbf{r}) j_{\ell'}(\alpha r)\cdot X_{LL'}(E) \qquad \text{for } r \geq S \ . \tag{3.25}$$

In the case of a muffin-tin potential, it can easily been shown that the sine and cosine matrices are diagonal

$$C_{LL'} = \cos\eta_\ell\cdot\delta_{LL'} \quad , \tag{3.26a}$$

with

$$\cos\eta_\ell = \alpha\cdot S^2 \left[n_\ell(\alpha r)\cdot\frac{d}{dr}\,\phi_L(E,\mathbf{r}) - \phi_L(E,\mathbf{r})\cdot\frac{d}{dr}\,n_\ell(\alpha r)\right]\Bigg|_{r=S} \quad , \tag{3.26b}$$

and

$$S_{LL'} = \sin\eta_\ell \cdot \delta_{LL'} \ , \tag{3.27a}$$

with

$$\sin\eta_\ell = \alpha \cdot S^2 [j_\ell(\alpha r) \cdot \frac{d}{dr} \phi_L(E,\mathbf{r}) - \phi_L(E,\mathbf{r}) \cdot \frac{d}{dr} j_\ell(\alpha r)] \Big|_{r=S} \ , \tag{3.27b}$$

where S is just the muffin-tin radius R_{mt}. Thus

$$X_{LL'} = \alpha \cdot \cot\eta_\ell \cdot \delta_{LL'} \ . \tag{3.28}$$

Equations (3.26) ∿ (3.28) are the results of the original derivation of KKR theory. In that derivation one has to assume that the potential is in the muffin-tin form. The band structure calculation based on (3.26) ∿ (3.28) is called the ordinary KKR calculation.

In practical calculations, the value of ℓ is taken only up to ℓ_{max} because the scattering of wave components with high angular momentum can be ignored.

3.3 COMPLEX CRYSTAL

A complex crystal structure is one in which there is more than one scatterer within a unit cell. An example of two atoms per unit cell is shown in Fig.1-4.

Let us assume that there are N scatterers (i.e. atoms) within a unit cell and $\mathbf{q}_i$, $i=1,2,\cdots,N$, denotes the position of ith scatterer. Then the potential $V(\mathbf{r})$ should be written as

$$V(\mathbf{r}) = \sum_{n}\sum_{i} v_i(\mathbf{r} - \mathbf{R}_n - \mathbf{q}_i) \ , \qquad (3.29)$$

with the assumption, as before, that the local potentials do not overlap each other. We can still follow the procedure used before but consider the scatterers within a unit cell separately.

Therefore, the incoming and outgoing waves associated with the ith scatterer within the nth unit cell are

$$\overset{o}{\phi}_{n,i}(E,\mathbf{r}_{n,i}) = \sum_{L} \overset{i}{N}_L(E,\mathbf{r}_{n,i})\cdot\xi_L^{n,i} \ , \qquad (3.30a)$$

$$\overset{i}{\phi}_{n,i}(E,\mathbf{r}_{n,i}) = \sum_{L} \overset{i}{J}_L(E,\mathbf{r}_{n,i})\cdot\eta_L^{n,i} \ , \qquad (3.30b)$$

respectively, where $\mathbf{r}_{n,i} = \mathbf{r} - \mathbf{R}_n - \mathbf{q}_i$. As in (3.8), we have

$$\eta_L^{n,i} = - \sum_{L'} X_{LL'}^{i}(E) \cdot \xi_{L'}^{n,i} \quad . \tag{3.31}$$

The matrix $\underline{X}^i$ is

$$\underline{X}^i(E) = \alpha \cdot \underline{C}^i(E) \cdot \underline{S}^i(E)^{-1} \quad , \tag{3.32}$$

where the sine and cosine matrices have the same form as (3.10) except additional superscripts and subscripts i

$$C_{LL'}^{i} = \alpha \cdot \int_{r_i \leq S_i} n_\ell(\alpha r_i) Y_L(\mathbf{r}_i) v(\mathbf{r}_i) \phi_{L'}^{i}(E, \mathbf{r}_i) d^3\mathbf{r} - \delta_{LL'} \quad , \tag{3.33a}$$

$$S_{LL'}^{i} = \alpha \cdot \int_{r_i \leq S_i} j_\ell(\alpha r_i) Y_L(\mathbf{r}_i) v(\mathbf{r}_i) \phi_{L'}^{i}(E, \mathbf{r}_i) d^3\mathbf{r} \quad . \tag{3.33b}$$

S_i is the radius of the bounding sphere of $\Omega(i)$ and $\phi_L^i(E,\mathbf{r}_i)$ is the solution of the differential equation

$$[-\nabla^2 + v_i(\mathbf{r} - \mathbf{q}_i)] \cdot f(E, \mathbf{r}_i) = E \cdot f(E, \mathbf{r}_i) \quad , \tag{3.33c}$$

with $\mathbf{r}_i = \mathbf{r} - \mathbf{q}_i$.

According to the multiple scattering theory, the incoming wave to the ith scatterer within the central unit cell can be written as

$$\phi_{i}^{i}(E,\mathbf{r}_{i}) = \sum_{n\neq 0} \phi_{n,i}^{o}(E,\mathbf{r}_{n,i}) + \sum_{n} \sum_{i'\neq i} \phi_{n,i'}^{o}(E,\mathbf{r}_{n,i'}) \ , \tag{3.34}$$

by suppressing the subscripts for n = 0. The second term of the above equation comes from the contribution of the scatterers other than the ith within all of the unit cells.

In terms of the incoming wave component of angular momentum L′ to the ith scatterer within the central unit cell, the expansion of the outgoing wave components of angular momentum L from the ith scatterer within the nth unit cell ($n \neq 0$) can be written as

$$\alpha \cdot N_{L}^{i}(E,\mathbf{r}_{n,i}) = \sum_{L'} J_{L'}^{i}(E,\mathbf{r}_{i}) \cdot A_{LL'}^{n,i}(E) \ . \tag{3.35}$$

Another expansion is about the outgoing wave component from the ith scatterer ($i' \neq i$) within any unit cell

$$\alpha \cdot N_{L}^{i'}(E,\mathbf{r}_{n,i'}) = \sum_{L'} J_{L'}^{i}(E,\mathbf{r}_{i}) \cdot A_{LL'}^{ii'}(E) \ . \tag{3.36}$$

Ignoring the near-field corrections, the expansion coefficients can be found as

$$A_{LL'}^{n,i}(E) = B_{LL'}^{n,i}(E) \ , \tag{3.37}$$

with

$$Y_L(\mathbf{r}_{n,i})n_\ell(\alpha r_{n,i}) = \sum_{L'} Y_{L'}(\mathbf{r}_i)j_{\ell'}(\alpha r_i)\cdot B_{LL'}^{n,i}(E) \quad , \tag{3.38}$$

and

$$A_{LL'}^{ii'}(E) = M_{LL'}^{ii'}(E) \quad , \tag{3.39}$$

with

$$Y_L(\mathbf{r}_{n,i'})n_\ell(\alpha r_{n,i'}) = \sum_{L'} Y_{L'}(\mathbf{r}_i)j_\ell(\alpha \mathbf{r}_i)\cdot M_{LL'}^{i'i} \quad . \tag{3.40}$$

The structure constants for complex crystal are defined as

$$B_{LL'}^{i}(E,\mathbf{k}) = \sum_{n\neq 0} e^{i\mathbf{k}\cdot\mathbf{R}n}.\, B_{LL'}^{n,i}(E) \quad , \tag{3.41a}$$

and

$$M_{LL'}^{ii'}(E,\mathbf{k}) = \sum_{n} e^{i\mathbf{k}\cdot\mathbf{R}n}.\, M_{LL'}^{ii'}(E) \quad . \tag{3.41b}$$

Obviously $B_{LL'}^{i}(E,\mathbf{k}) = B_{LL'}(E,\mathbf{k})$, because of the translation symmetry in a perfect crystal. The explicit expression for the structure constants $M_{LL'}^{ii'}(E,\mathbf{k})$ is also available in the literatures[11,23]. Combining (3.32) with (3.29), (3.30) and structure constants obtained above, and considering

$$\xi_L^{n,i} = e^{i\mathbf{k}\cdot\mathbf{R}n}\cdot\xi_L^{i} \quad , \tag{3.42}$$

we finally have a set of homogeneous equations for ξ_L^{i}

$$\sum_{i'}\sum_{L'}\left[\left(X_{LL}^{i}(E) + B_{LL'}(E,\mathbf{k})\right)\cdot\delta_{ii'} + M_{LL'}^{ii'}(E,\mathbf{k})\right]\cdot\xi_{L'}^{i'} = 0 \; , \tag{3.43}$$

with the definition

$$M_{LL'}^{ii}(E,\mathbf{k}) = 0 \; . \tag{3.44}$$

The coefficients ξ_L^{i} have nontrivial solutions only if

$$\det\left[\; \underline{X}(E) + \underline{B}(E,k) + M(E) \;\right]$$

$$= \det\begin{pmatrix} \underline{X}^1 + \underline{B} & \underline{M}^{1\,2} & \cdots & \underline{M}^{1\,n} \\ \underline{M}^{2\,1} & \underline{X}^2 + \underline{B} & \cdots & \underline{M}^{2\,n} \\ \underline{M}^{3\,1} & \underline{M}^{3\,2} & \cdots & \underline{M}^{3\,n} \\ \vdots & \vdots & & \vdots \\ \underline{M}^{n\,1} & \underline{M}^{n\,2} & \cdots & \underline{X}^n + \underline{B} \end{pmatrix}$$

$$= 0 \tag{3.45}$$

Compared with the simple crystal, the size of above matrix is N x N times larger.

In the case of muffin-tin potential, sine and cosine matrices will be in the diagonal form

$$C^{i}_{LL'}(E) = \cos\eta^{i}_{\ell}\cdot\delta_{LL'} \tag{3.46a}$$

with

$$\cos\eta^{i}_{\ell} = \alpha\cdot S_i^{2}[n_\ell(\alpha r_i)\cdot\frac{d}{dr_i}\phi_\ell(E,\mathbf{r}_i) - \phi_\ell(E,\mathbf{r}_i)\cdot\frac{d}{dr_i}n_\ell(\alpha r_i)]\Big|_{r_i=S_i} , \tag{3.46b}$$

and

$$S^{i}_{LL'}(E) = \sin\eta^{i}_{\ell}\cdot\delta_{LL'} \tag{3.47a}$$

with

$$\sin\eta^{i}_{\ell} = \alpha\cdot S_i^{2}[j_\ell(\alpha r_i)\cdot\frac{d}{dr_i}\phi_\ell(E,\mathbf{r}_i) - \phi_\ell(E,\mathbf{r}_i)\cdot\frac{d}{dr_i}j_\ell(\alpha r_i)]\Big|_{r_i=S_i} , \tag{3.47b}$$

therefore

$$X^{i}_{LL'} = \alpha\cdot\cot\eta^{i}_{\ell}\cdot\delta_{LL'} \ . \tag{3.48}$$

The ordinary KKR calculation for complex crystals are based on equations (3.46) ∿ (3.48).

CHAPTER 4

QKKR THEORY

4.1 INTRODUCTION

As in the last chapter, We shall treat simple crystals first. The generalization to complex crystals will be given in section 4.3.

Notice that an alternate form of KKR equation can be obtained by defining the column matrix $\underline{d}^{\lambda}(\mathbf{k})$ as following

$$\underline{d}(\mathbf{k}) = \underline{S}^{-1}(E)\cdot\underline{\xi}(\mathbf{k}) \ . \qquad (4.1)$$

Therefore the equation (3.21) becomes

$$\sum_{L'} P_{LL'}(E,\mathbf{k})\cdot d_{L'}(\mathbf{k}) = 0 \ , \qquad (4.2)$$

with

$$\underline{P}(E,\mathbf{k}) = \alpha\cdot\underline{C}(E) + [\underline{B}(E,\mathbf{k}) + \underline{N}(E,\mathbf{k})]\cdot\underline{S}(E) \ . \qquad (4.3)$$

Equation (3.22) becomes

$$\det \underline{P}(E,\mathbf{k}) = 0 \; . \tag{4.4}$$

This is a very useful equation because it eliminates the singular points of the sine matrix $\underline{S}(E)$ so that they won't affect our looking for the eigenvalues with the KKR method through the equation (4.4). On the other hand this equation is important in the QKKR theory, as discussed in the following.

4.2 QKKR THEORY

The starting point of QKKR theory is to consider the fact that when the boundaries of the regions Ω_n approach to the boundaries of the Wigner-Seitz cells, the volume of the interstitial area goes to zero, so that the value of the constant interstitial potential V_{con} becomes an irrelevant parameter. In this case the local potential should be written as:

$$v'(\mathbf{r}_n) = v(\mathbf{r}_n)\cdot\sigma(\mathbf{r}_n) \quad , \tag{4.5}$$

where $\sigma(\mathbf{r}_n)$ is a three dimensional step function defined as:

$$\sigma(\mathbf{r}_n) = \begin{cases} 1 & \text{if } \mathbf{r}_n \in \Omega_n \\ 0 & \text{if } \mathbf{r}_n \notin \Omega_n \quad . \end{cases} \tag{4.6}$$

Let us define a so-called pivotal energy E_0, which relates to $V_{con}=0$. Since V_{con} is an irrelevant parameter, we can choose it to be some value other than zero, such as

$$\Delta^{\lambda}(\mathbf{k}) = E^{\lambda}(\mathbf{k}) - E_0 \quad . \tag{4.7}$$

This leaves the one-electron Schrödinger equation

$$[\ -\nabla^2 + V(\mathbf{r})\ ]\cdot\Psi^{\lambda}_{\mathbf{k}}(\mathbf{r}) = E^{\lambda}(\mathbf{k})\cdot\Psi^{\lambda}_{\mathbf{k}}(\mathbf{r}) \quad , \tag{4.8}$$

unchanged, where the one-electron potential is

$$V(\mathbf{r}) = \sum_n v'(\mathbf{r}_n) \tag{4.9}$$

$$= \sum_n v(\mathbf{r}_n) \quad .$$

As discussed before (in section 1.2), we can subtract $\Delta^{\lambda}(\mathbf{k})$ from the local potentials $v'(\mathbf{r}_n)$ which will shift the energy $E^{\lambda}(\mathbf{k})$ back to E_0 while V_{con} remains zero. The local potential is replaced by

$$v^{\Delta}(\mathbf{r}_n) = (\ v(\mathbf{r}_n) - \Delta^{\lambda}(\mathbf{k})\ )\cdot\sigma(\mathbf{r}) \ , \tag{4.10}$$

and the equivalent one-electron Schrödinger equation is

$$[\ -\nabla^2 + V^{\Delta}(\mathbf{r})\ ]\cdot\Psi^{\lambda}_{\mathbf{k}}(\mathbf{r}) = E_0\cdot\Psi^{\lambda}_{\mathbf{k}}(\mathbf{r}) \quad , \tag{4.11}$$

where

$$V^{\Delta}(\mathbf{r}) = \sum_n v^{\Delta}(\mathbf{r}_n) \quad . \tag{4.12}$$

Thus, we can still apply the equations derived in the last chapter with $v(\mathbf{r})$ replaced by $v^{\Delta}(\mathbf{r})$.

Therefore the Bloch wave function can be written as

$$\Psi_{\mathbf{k}}^{\lambda}(\mathbf{r}) = \sum_{L} \phi_{L}^{\Delta}(E_0,\mathbf{r})\cdot d_{L}^{\lambda}(\mathbf{k}) \quad , \tag{4.13}$$

where

$$\phi_{L}^{\Delta}(E_0,\mathbf{r}) = Y_L(\mathbf{r})j_{\ell}(\alpha_0 r) + \int_{|\mathbf{r}'|\leq|\mathbf{r}|} G(E_0,\mathbf{r},\mathbf{r}')v^{\Delta}(\mathbf{r}')\phi_{L}^{\Delta}(E_0,\mathbf{r}')d^3\mathbf{r}' \quad , \tag{4.14}$$

with

$$\alpha_0 = \sqrt{E_0} \quad , \tag{4.15}$$

$G(E_0,\mathbf{r},\mathbf{r}')$ is given by (3.11b), and $d_{L}^{\lambda}(\mathbf{k})$ are solutions of

$$\sum_{L'} P_{LL'}^{\Delta}(E_0,\mathbf{k})\cdot d_{L'}(\mathbf{k}) = 0 \quad , \tag{4.16}$$

in which the matrix (ignoring near-field corrections)

$$\underline{P}^{\Delta}(E_0,\mathbf{k}) = \alpha_0\underline{C}^{\Delta}(E_0) + \underline{B}(E_0,\mathbf{k})\cdot\underline{S}^{\Delta}(E_0) \quad . \tag{4.17}$$

The sine and cosine matrices can be found by evaluating the following integral equations:

$$C_{LL'}^{\Delta}(E_0) = \alpha_0 \int n_{\ell}(\alpha_0 r)Y_L(\mathbf{r})v^{\Delta}(\mathbf{r}) \times \phi_{L'}^{\Delta}(E_0,\mathbf{r})d^3\mathbf{r} - \delta_{LL'}, \tag{4.18a}$$

$$S^{\Delta}_{LL'}(E_0) = \alpha_0 \int j_{\ell}(\alpha_0 r) Y_L(\mathbf{r}) v^{\Delta}(\mathbf{r}) \times \phi^{\Delta}_{L'}(E_0, \mathbf{r}) d^3\mathbf{r} \qquad (4.18b)$$

Notice that the matrices $\underline{C}^{\Delta}(E_0)$ and $\underline{S}^{\Delta}(E_0)$ are entire functions of Δ. Therefore we can expand them as Taylor series in Δ, so that

$$\underline{C}^{\Delta}(E_0) = \underline{C}^{(0)}(E_0)+\underline{C}^{(1)}\cdot\Delta+\underline{C}^{(2)}(E_0)\cdot\Delta^2+\cdots , \qquad (4.19a)$$

$$\underline{S}^{\Delta}(E_0) = \underline{S}^{(0)}(E_0)+\underline{S}^{(1)}\cdot\Delta+\underline{S}^{(2)}(E_0)\cdot\Delta^2+\cdots . \qquad (4.19b)$$

Inserting these equations into (4.14) with assuming that the near field corrections can be ignored, i.e., $\underline{N}^{\Delta}(E_0,\mathbf{k})=0$, we have

$$\underline{P}^{\Delta}(E_0,\mathbf{k}) = \underline{H}(\mathbf{k}) - \underline{O}(\mathbf{k})\cdot\Delta + \underline{A}(\mathbf{k})\cdot\Delta^2 + \cdots , \qquad (4.20)$$

where

$$\underline{H}(\mathbf{k}) = \alpha_0\ \underline{C}^{(0)}(E_0) + \underline{B}(E_0,\mathbf{k})\cdot\underline{S}^{(0)}(E_0) , \qquad (4.21a)$$

$$\underline{O}(\mathbf{k}) = -\alpha_0\ \underline{C}^{(1)}(E_0) - \underline{B}(E_0,\mathbf{k})\cdot\underline{S}^{(1)}(E_0) , \qquad (4.21b)$$

$$\underline{A}(\mathbf{k}) = \alpha_0\ \underline{C}^{(2)}(E_0) + \underline{B}(E_0,\mathbf{k})\cdot\underline{S}^{(2)}(E_0) . \qquad (4.21c)$$

If we define the matrices

$$\underline{\epsilon}(\mathbf{k}) = \underline{O}(\mathbf{k})^{-1}\cdot\underline{H}(\mathbf{k}) \quad , \tag{4.22a}$$

$$\underline{D}(\mathbf{k}) = \underline{A}(\mathbf{k})^{-1}\cdot\underline{O}(\mathbf{k}) \quad , \tag{4.22b}$$

and ignore all terms beyond the quadratic one in the equations (4.17a&b), the equation (4.18) can be written in the form as

$$[\ \Delta^2 - \underline{D}(\mathbf{k})\cdot(\Delta - \underline{\epsilon}(\mathbf{k}))\ ]\cdot\underline{d}(\mathbf{k}) = 0 \quad . \tag{4.23}$$

The elements of the column matrix $\underline{d}(\mathbf{k})$ are the coefficients $d_L^{\lambda}(\mathbf{k})$. A column matrix $\underline{h}(\mathbf{k})$ with elements, related to the band λ, that will be called $h_L^{\lambda}(\mathbf{k})$ is defined as

$$\underline{h}(\mathbf{k}) = [\ \Delta - \underline{\epsilon}(\mathbf{k})\ ]\cdot\underline{d}(\mathbf{k}) \quad . \tag{4.24}$$

Coupling this equation with (4.22a&b) and (4.23) leads to the important matrix equation of QKKR theory

$$\begin{bmatrix} \Delta\cdot\underline{I} + \underline{\epsilon} - \underline{D} & \underline{\epsilon}^2 \\ -\underline{I} & \Delta\cdot\underline{I} - \underline{\epsilon} \end{bmatrix}\cdot\begin{bmatrix} \underline{h} \\ \underline{d} \end{bmatrix} = 0 \quad , \tag{4.25a}$$

which has the form of a standard eigenvalue equation, i.e.,

$$\left(\begin{bmatrix} \Delta\cdot\underline{I} & 0 \\ 0 & \Delta\cdot\underline{I} \end{bmatrix} - \begin{bmatrix} \underline{D} - \underline{\epsilon} & -\underline{\epsilon}^2 \\ \underline{I} & \underline{\epsilon} \end{bmatrix} \right) \cdot \begin{bmatrix} \underline{h} \\ \underline{d} \end{bmatrix} = 0 \quad , \qquad (4.25b)$$

and can be evaluated by diagonalizing the matrix $\underline{Q}(\mathbf{k})$

$$\underline{Q} = \begin{bmatrix} \underline{D} - \underline{\epsilon} & -\underline{\epsilon}^2 \\ \underline{I} & \underline{\epsilon} \end{bmatrix} \quad , \qquad (4.26)$$

so that the ordinary energy eigenvalues will be

$$E^{\lambda}(\mathbf{k}) = \Delta^{\lambda}(\mathbf{k}) + E_0 \quad . \qquad (4.27)$$

It can easily be concluded that, if the angular momenta are considered only up to ℓ_{max}, the dimension of the matrices $\underline{S}^{\Delta}$ and $\underline{C}^{\Delta}$ is $(\ell_{max}+1)\times(\ell_{max}+1)$, while that of the matrix $\underline{Q}$ is $2(\ell_{max}+1)\times 2(\ell_{max}+1)$.

4.3 COMPLEX CRYSTAL

It is very easy to carry out the extension to the complex crystal if we carefully add those subscripts and superscripts, which represent the index of atoms in a unit cell, to the functions and matrices in the above equations.

Thus the Bloch function is given by

$$\Psi_{\mathbf{k}}^{\lambda}(\mathbf{r}) = \sum_{i,L} \phi_{L,i}^{\Delta}(E_0,\mathbf{r}_i)\cdot d_L^{\lambda}(\mathbf{k}) \quad , \tag{4.28}$$

where

$$\phi_{L,i}^{\Delta}(E_0,\mathbf{r}_i) = Y_L(\mathbf{r}_i)j_\ell(\alpha r_i) \; + \int_{r_i'\leq r_i} G(E_0,r_i,r_i')\cdot v_i^{\Delta}(\mathbf{r}_i') \times \phi_{L,i}^{\Delta}(E_0,\mathbf{r}_i')\cdot d^3r_i' \quad , \tag{4.29}$$

and $d_{L,i}^{\lambda}(\mathbf{k})$ are solutions of the set of equations

$$\sum_{i'}\sum_{L'} P_{LL'}^{\Delta,ii'}(E_0,\mathbf{k})\cdot d_{L',i'}(\mathbf{k}) = 0 \; . \tag{4.30}$$

With the assumption that the near-field corrections can be ignored,

$$\underline{P}^{\Delta}(E_0,\mathbf{k}) = \alpha_0\cdot\underline{C}^{\Delta}(E_0) + [\underline{B}(E_0,\mathbf{k}) + \underline{M}(E_0,\mathbf{k})]\cdot\underline{S}^{\Delta}(E_0)$$

$$= \underline{H}(\mathbf{k}) - \underline{O}(\mathbf{k})\cdot\Delta + \underline{A}(\mathbf{k})\cdot\Delta^2 \quad . \tag{4.31}$$

The structure constant matrices $\underline{B}$ and $\underline{M}$ are given in the literatures mentioned in the last chapter. The matrices $\underline{H}$, $\underline{O}$ and $\underline{A}$ are of the form

$$\underline{H}(\mathbf{k}) = \alpha_0 \; \underline{C}^{(0)}(E_0) + [\underline{B}(E_0,\mathbf{k}) + \underline{M}(E_0,\mathbf{k})]\cdot\underline{S}^{(0)}(E_0) \tag{4.32a}$$

$$\underline{O}(\mathbf{k}) = -\alpha_0 \; \underline{C}^{(1)}(E_0) - [\underline{B}(E_0,\mathbf{k}) + \underline{M}(E_0,\mathbf{k})]\cdot\underline{S}^{(1)}(E_0) \tag{4.32b}$$

$$\underline{A}(\mathbf{k}) = \alpha_0 \; \underline{C}^{(2)}(E_0) + [\underline{B}(E_0,\mathbf{k}) + \underline{M}(E_0,\mathbf{k})]\cdot\underline{S}^{(2)}(E_0) \quad , \tag{4.32c}$$

in which the sine and cosine matrices are given by

$$\begin{aligned} C_{LL'}^{\Delta,ii'}(E_0) &= \delta_{ii'}\cdot[\; \alpha_0\cdot\int_{r_i'\le r_i} Y_L(\mathbf{r}_i')\, n_\ell(\alpha_0 r_i')\, v_i^{\Delta}(\mathbf{r}_i') \\ &\qquad\qquad \times \phi_{L'}^{\Delta,i}(E_0,\mathbf{r}_i')\, d^3\mathbf{r}_i' - \delta_{LL'} \;] \\ &= \delta_{ii'}\cdot[\; C_{LL'}^{(0),i}(E_0) + \Delta\cdot C_{LL'}^{(1),i}(E_0) \\ &\qquad\qquad + \Delta^2\cdot C_{LL'}^{(2),i}(E_0) \;] \quad , \end{aligned} \tag{4.30a}$$

$$S_{LL'}^{\Delta,ii'}(E_0) = \delta_{ii'}\cdot\alpha_0\cdot\int_{r_i'\le r_i} Y_L(\mathbf{r}_i')\, j_\ell(\alpha_0 r_i')\, v_i^{\Delta}(\mathbf{r}_i')$$

$$\times \phi_{L'}^{\Delta,i}(E_0,\mathbf{r}_i')d^3\mathbf{r}_i'$$

$$= \delta_{ii'}\cdot[\ S_{LL'}^{(0),i}(E_0) + \Delta\cdot S_{LL'}^{(1),i}(E_0) + \Delta^2\cdot S_{LL'}^{(2),i}(E_0)\ ]\ . \tag{4.30b}$$

Equations (4.22) ∿ (4.27) are in the same form except the dimensions of these matrices are N × N times larger.

4.4 THE COMPARISON WITH KKR METHOD

The most important advantage of QKKR method is its much smaller time consumption in practical calculations. The QKKR theory provides a very effective method that can be used to find all the energy eigenvalues for a certain **k** vector by diagonalizing the matrix $\underset{\sim}{Q}$, which takes the same time as calculating one determinant. The accuracy of the QKKR method depends on the range of Δ values, since we include only up to the quadratic terms in the expansions of sine and cosine matrices. Usually, we choose E_0 around the middle of the energy range in which we are most interested, so that the energy bands within that range, calculated from the equation (4.27), will have enough accuracy. Obviously, the closer to the E_0, the more accurate the energy eigenvalue will be.

The QKKR calculations for some simple metals have been carried out by Faulkner and demonstrate great accuracy when compared with the results from the KKR method.

In chapter 6, I will provide the results of calculations for a complex crystal.

CHAPTER 5

STEP FUNCTION

5.1 INTRODUCTION

The most difficult problem in the QKKR calculation is evaluating the elements of the sine and cosine matrices. In order to find the expansion coefficients of $S^{\Delta}(E_0)$ and $C^{\Delta}(E_0)$ on Δ, we need to give Δ a trial value, such as δ. For a certain atom in the unit cell with origin of the coordinates set on it

$$C^{\delta}_{L,L'}(E_0) = \alpha_0 \cdot \int n_{\ell}(\alpha_0 r) Y_L(\mathbf{r}) v^{\delta}(\mathbf{r}) \cdot \phi^{\delta}_{L'}(E_0, \mathbf{r}) \, d^3\mathbf{r} - \delta_{LL'}, \tag{5.1a}$$

$$S^{\delta}_{L,L'}(E_0) = \alpha_0 \cdot \int j_{\ell}(\alpha_0 r) Y_L(\mathbf{r}) v^{\delta}(\mathbf{r}) \cdot \phi^{\delta}_{L'}(E_0, \mathbf{r}) \, d^3\mathbf{r}, \tag{5.1b}$$

where I drop the superscripts or subscripts 'i' representing the type of atom for convenience, and the integrations are carried over the sub-cell.

Expanding the local potential $v^{\delta}(\mathbf{r})$ in terms of the real spherical harmonics yields

$$v^{\delta}(\mathbf{r}) = \sum_{L} v_{L}^{\delta}(r)\cdot Y_{L}(\mathbf{r}) \quad , \tag{5.2}$$

where

$$v_{L}^{\delta}(r) = \int do \; Y_{L}(\mathbf{r})\cdot v^{\delta}(\mathbf{r}) \quad . \tag{5.3}$$

Thus the equations (5.1a&b) become

$$C_{L,L'}^{\delta}(E_0) = \alpha_0 \sum_{L'',L_0} \int_0^S r^2\cdot dr \; n_{\ell}(\alpha_0 r) v_{L''}^{\delta}(r) \phi_{L_0 L'}^{\delta}(E_0,r) \times g_{L,L_0}^{L''} - \delta_{LL'} \quad , \tag{5.4a}$$

$$S_{L,L'}^{\delta}(E_0) = \alpha_0 \sum_{L'',L_0} \int_0^S r^2\cdot dr \; j_{\ell}(\alpha_0 r) v_{L''}^{\delta}(r) \phi_{L_0 L'}^{\delta}(E_0,r) \times g_{L,L_0}^{L''} \quad , \tag{5.4b}$$

defining

$$g_{L,L_0}^{L''} = \int do \; Y_{L}(\mathbf{r}) Y_{L''}(\mathbf{r}) Y_{L_0}(\mathbf{r}) , \tag{5.5}$$

which are called Gaunt factors, and

$$\begin{aligned} \phi_{L_0 L'}^{\delta}(E_0,r) &= \int do \; Y_{L_0}(\mathbf{r}) \phi_{L'}^{\delta}(E_0,\mathbf{r}) \\ &= j_{\ell_0}(\alpha_0 r)\cdot \delta_{L_0 L'} + \sum_{L'',L} \int_0^r r'^2 dr' G_{\ell_0}(E_0,r,r') \end{aligned}$$

$$\times\ v^{\delta}_{L''}(r')\,\phi^{\delta}_{LL'}(E_0,r')\cdot g^{L''}_{L_0,L}$$

$$= j_{\ell_0}(\alpha_0 r)\,C^{\delta}_{L_0,L'}(E_0,r) + n_{\ell_0}(\alpha_0 r)\,S^{\delta}_{L_0,L'}(E_0,r), \tag{5.6}$$

in which

$$G_{\ell}(E_0,r,r') = -\alpha_0\cdot[j_{\ell}(\alpha_0 r)\,n_{\ell}(\alpha_0 r') - n_{\ell}(\alpha_0 r)\,j_{\ell}(\alpha_0 r')], \tag{5.7}$$

$$C^{\delta}_{L_0,L'}(E_0,r) = \alpha_0 \sum_{L,L''} \int_0^r r'^2 dr'\, n_{\ell_0}(\alpha_0 r')\,v^{\delta}_{L''}(r') \times \phi^{\delta}_{LL'}(E_0,r')\cdot g^{L''}_{L_0,L} - \delta_{L_0 L'}, \tag{5.8a}$$

$$S^{\delta}_{L_0,L'}(E_0,r) = \alpha_0 \sum_{L,L''} \int_0^r r'^2 dr'\, j_{\ell_0}(\alpha_0 r')\,v^{\delta}_{L''}(r') \times \phi^{\delta}_{LL'}(E_0,r')\cdot g^{L''}_{L_0,L}\,. \tag{5.8b}$$

Comparing (5.8a&b) with (5.4a&b), one has

$$C^{\delta}_{L_0,L'}(E_0) = C^{\delta}_{L_0,L'}(E_0,r)\Big|_{r\,=\,S}\,, \tag{5.9a}$$

$$S^{\delta}_{L_0,L'}(E_0) = S^{\delta}_{L_0,L'}(E_0,r)\Big|_{r\,=\,S}\,. \tag{5.9b}$$

Therefore, if the function $v^{\delta}_{L}(r)$ is known, the sine and cosine matrices for certain value of δ can be evaluated by iterating the equations (5.6) ∿ (5.9).

The expansion coefficients of the matrices will be found as follows

$$\underline{C}^{(0)}(E_0) = \underline{C}^{\delta}(E_0)\Big|_{\delta = 0}, \tag{5.10a}$$

$$\underline{C}^{(1)}(E_0) = \left(\underline{C}^{\delta}(E_0)\Big|_{\delta = \beta} - \underline{C}^{\delta}(E_0)\Big|_{\delta = -\beta}\right) / 2 , \tag{5.10b}$$

$$\underline{C}^{(2)}(E_0) = \left(\underline{C}^{\delta}(E_0)\Big|_{\delta = \beta} + \underline{C}^{\delta}(E_0)\Big|_{\delta = -\beta} - \underline{C}^{\delta}(E_0)\Big|_{\delta = 0}\right) / 2 , \tag{5.10c}$$

$$\underline{S}^{(0)}(E_0) = \underline{S}^{\delta}(E_0)\Big|_{\delta = 0} , \tag{5.11a}$$

$$\underline{S}^{(1)}(E_0) = \left(\underline{S}^{\delta}(E_0)\Big|_{\delta = \beta} - \underline{S}^{\delta}(E_0)\Big|_{\delta = -\beta}\right) / 2 , \tag{5.11b}$$

$$\underline{S}^{(2)}(E_0) = \left(\underline{S}^{\delta}(E_0)\Big|_{\delta = \beta} + \underline{S}^{\delta}(E_0)\Big|_{\delta = -\beta} - \underline{S}^{\delta}(E_0)\Big|_{\delta = 0}\right) / 2 . \tag{5.11c}$$

Assuming that

$$v(\mathbf{r}) - \delta = \sum_{L} Y_L(\mathbf{r}) \cdot u_L^{\delta}(r) , \tag{5.12}$$

one has

$$\begin{aligned} v_L^{\delta}(r) &= \int do\ Y_L(\mathbf{r})\cdot[v(\mathbf{r}) - \delta]\cdot\sigma(\mathbf{r}) \\ &= \sum_{L'} [\int do\ Y_L(\mathbf{r})Y_{L'}(\mathbf{r})\sigma(\mathbf{r})]\cdot u_{L'}^{\delta}(r) \\ &= \sum_{L'} \sigma_{LL'}(r)\cdot u_{L'}^{\delta}(r) \ , \end{aligned} \tag{5.13}$$

where

$$u_{L'}^{\delta}(r) = \int do\ Y_{L'}(\mathbf{r})\cdot[v(\mathbf{r}) - \delta] \ , \tag{5.14}$$

$$\sigma_{LL'}^{\delta}(r) = \int do\ Y_L(\mathbf{r})Y_{L'}(\mathbf{r})\cdot\sigma(\mathbf{r}) \ . \tag{5.15}$$

Hence, the evaluation of the integration in (5.15) becomes a major problem in QKKR theory. The difficulty arises from the fact that the step function $\sigma(\mathbf{r})$ equals 1 within the polyhedron, which is a Wigner-Seitz cell in the case of simple crystals or a sub-cell in the case of complex crystals. The development of the technique for doing this integral for complex crystals is reported in this thesis for the first time.

Notice that, if one expands $\sigma(\mathbf{r})$ as

$$\sigma(\mathbf{r}) = \sum_{L} Y_L(\mathbf{r})\cdot\sigma_L(r) \ , \tag{5.16a}$$

(5.15) becomes

$$\sigma_{LL'}(r) = \sum_{L''} \sigma_{L''}(r) \cdot g_{L,L'}^{L''} \quad , \qquad (5.16b)$$

where

$$\sigma_{L''}(r) = \int do \;\; Y_{L''}(\mathbf{r}) \cdot \sigma(\mathbf{r}) \quad . \qquad (5.17)$$

Therefore it needs to develop an effective method for evaluating $\sigma_L(r)$.

5.2 TECHNIQUE FOR THE EXPANSION OF $\sigma(\mathbf{r})$

First of all, let us study the geometrical properties of the polyhedron. Notice that its boundaries are composed of several planes with certain distances from the center, where the atom is located. The distances are determined according to the muffin-tin radii $R_{mt}(i)$ (with $i=1,2,\cdots,N$) of the atoms within the unit cell and the lattice constants. An example was shown before by Fig.1-4.

Assume that the nth boundary plane is represented by P_n, which has a normal unit vector τ_n directed outward from the polyhedron and has a distance d_n from the center of the polyhedron. The position vector of the associated neighboring atom on the opposite side of the plane is denoted by $\mathbf{R}_n$, which can be written as

$$\begin{aligned}\mathbf{R}_n &= R_n \cdot \tau_n \\ &= X_n \cdot \mathbf{e}_x + Y_n \cdot \mathbf{e}_y + Z_n \cdot \mathbf{e}_z \ . \end{aligned} \qquad (5.18)$$

Obviously, any point inside the polyhedron must satisfy the following equation

$$\mathbf{r} \cdot \tau_n \le d_n \qquad \text{for } n = 1,2,\cdots,N_p \ , \qquad (5.19)$$

where $\mathbf{r}$ is a position vector whose origin is at the center, and N_p is the total number of boundary planes. Because of

(5.18) the equation (5.19) can be written in an alternate form as

$$\mathbf{r}\cdot\mathbf{R}_n \le R_n\cdot d_n \ . \tag{5.20}$$

A spherical surface with radius r that is concentric with the polyhedron will intersect its boundaries unless r less than R_{mt}, the radius of its inscribed sphere or r larger than S, the radius of its circumscribed sphere. The intersection points can be found by equating both side of equation (5.20)

$$\begin{aligned}\mathbf{r}\cdot\mathbf{R}_n &= R_n\cdot d_n \\ &= Z_n\cdot r\cdot\cos\theta + \cos\alpha_n(r,\theta)\cdot\sqrt{X_n^2 + Y_n^2}\cdot r\cdot\sin\theta \ ,\end{aligned} \tag{5.21}$$

where θ is the polar angle and $\alpha_n(r,\theta)$ is the difference between the azimuthal angles of **r** and $\mathbf{R}_n$. If we denote Φ_n as the azimuthal angle of $\mathbf{R}_n$, $\Phi_n + \alpha_n(r,\theta)$ is the azimuthal angle of **r** representing the intersection point with the nth plane for a given polar angle. These angles can be calculated by

$$\cos\Phi_n = \frac{X_n}{\sqrt{X_n^2 + Y_n^2}} \ , \tag{5.22a}$$

and

$$\alpha_n(r,\theta) = \pm \left| \cos^{-1} \frac{d_n \cdot R_n - Z_n \cdot r \cdot \cos\theta}{\sqrt{X_n^2 + Y_n^2} \cdot r \cdot \sin\theta} \right| . \tag{5.22b}$$

Without loosing any generality, one may assume that

$$\left\{ \begin{aligned} &\Phi_n < \Phi_{n+1} , &(5.23a) \\ &\Phi_{N_p+1} = 2\pi + \Phi_1 . &(5.23b) \end{aligned} \right.$$

Therefore the necessary and sufficient condition for a point on the spherical surface locating inside the polyhedron is that the azimuth angle ϕ associated with this point must satisfies

$$\Phi_n + |\alpha_n(r,\theta)| \leq \phi \leq \Phi_{n+1} - |\alpha_{n+1}(r,\theta)| . \tag{5.24}$$

Thus, the expansion coefficients of the step function is calculated from

$$\sigma_L(r) = \int do \; Y_L(\mathbf{r}) \cdot \sigma(\mathbf{r})$$

$$= \int_0^{\pi} \sin\theta \; d\theta \cdot \int_0^{2\pi} d\phi \; Y_L(\mathbf{r}) \cdot \sigma(\mathbf{r})$$

$$
= \begin{cases}
A_L \int_0^\pi d\theta\cdot\sin\theta\cdot P_\ell^m(\cos\theta)\sum_{n=1}^{N_p}\frac{1}{m}\cdot\gamma_n(\theta)\cdot\Big\{\sin[m\cdot(\Phi_{n+1} \\
\quad -\,|\alpha_{n+1}(r,\theta)|)] - \sin[m\cdot(\Phi_n + |\alpha_n(r,\theta)|)]\Big\} \\
\qquad\qquad\qquad\qquad\qquad\qquad \text{if} \quad m > 0, \\
A_L \int_0^\pi d\theta\cdot\sin\theta\cdot P_\ell^m(\cos\theta)\sum_{n=1}^{N_p}\frac{1}{m}\cdot\gamma_n(\theta)\cdot\Big\{\cos[m\cdot(\Phi_{n+1} \\
\quad -\,|\alpha_{n+1}(r,\theta)|)] - \cos[m\cdot(\Phi_n + |\alpha_n(r,\theta)|)]\Big\} \\
\qquad\qquad\qquad\qquad\qquad\qquad \text{if} \quad m < 0, \\
A_L \int_0^\pi d\theta\cdot\sin\theta\cdot P_\ell(\cos\theta)\sum_{n=1}^{N_p}\frac{1}{m}\cdot\gamma_n(\theta)\cdot\Big\{[\Phi_{n+1} \\
\quad -\,|\alpha_{n+1}(r,\theta)|] - [\Phi_n + |\alpha_n(r,\theta)|]\Big\}\;, \\
\qquad\qquad\qquad\qquad\qquad\qquad \text{if} \quad m = 0,
\end{cases} \tag{5.25a}
$$

which takes on the limiting values

$$
\sigma_L(r) = \begin{cases}
\sqrt{4\pi} & \text{if } \; r \le R_{mt} \; \text{ and } \; \ell = 0 \\
0 & \text{if } \; r \le R_{mt} \; \text{ and } \; \ell \ne 0 \; \text{ or } \; r > S,
\end{cases} \tag{5.25b}
$$

where A_L are the constant coefficients of the real spherical harmonics (see Appendix II), and $\gamma_n(\theta)$ is defined as

$$\gamma_n(\theta) = \begin{cases} 1 & \text{if } \Phi_n + |\alpha_n(r,\theta)| < \Phi_{n+1} - |\alpha_{n+1}(r,\theta)| \\ 0 & \text{if } \Phi_n + |\alpha_n(r,\theta)| \geq \Phi_{n+1} - |\alpha_{n+1}(r,\theta)| , \end{cases} \tag{5.26}$$

in order to eliminate the case

$$\Phi_n + |\alpha_n(r,\theta)| \geq \Phi_{n+1} - |\alpha_{n+1}(r,\theta)| , \tag{5.27}$$

during the integrations over ϕ in (5.25). The final integrations over θ in (5.25) can be carried through by numerical methods without any difficulty.

CHAPTER 6

COMPUTATIONS AND RESULTS

6.1 INTRODUCTION

All of the basic equations have been displayed or derived in previous chapters. Now it is ready to carry out the calculations for a given crystal. The sample material I considered is PdH, which is a complex crystal with two atoms per unit cell and has the same lattice structure as NaCl (see Fig. 6-1.).

The lattice constant a_0 and the muffin-tin radii for both Pd and H atoms are, in atomic units,

$a_0 = 7.61570$,

$R_{mt}(Pd) = 2.47510$,

$R_{mt}(H) = 1.33275$,

$S(Pd) = 3.29769$,

$S(H) = 2.30839$.

The unit cell and sub-cells of PdH are shown in Fig.6-2 so that the step functions for both atoms, i.e. $\sigma_{Pd}(\mathbf{r})$ and

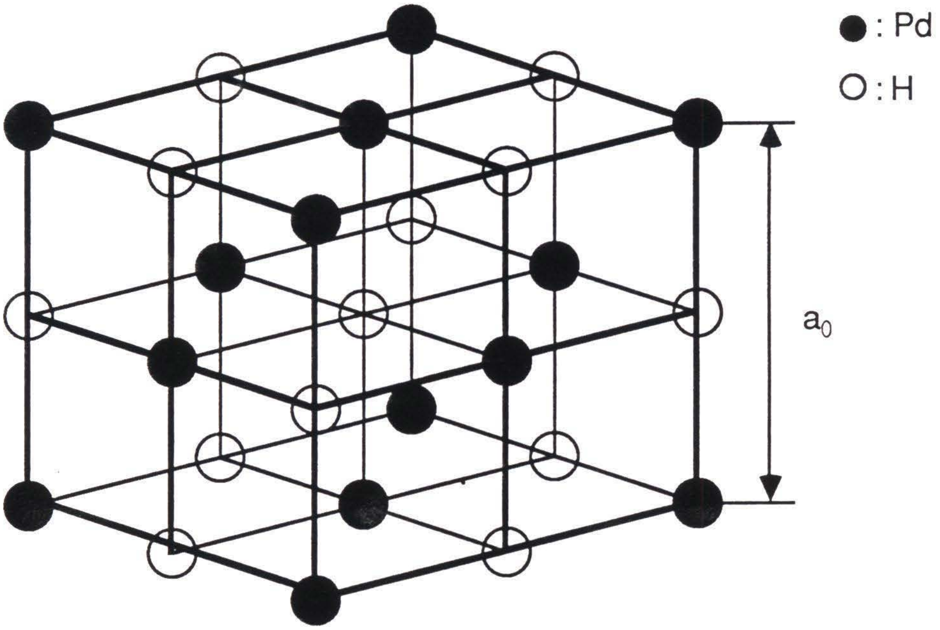

Fig. 6-1. The crystal structure of PdH is FCC type. It has two atoms per unit cell.

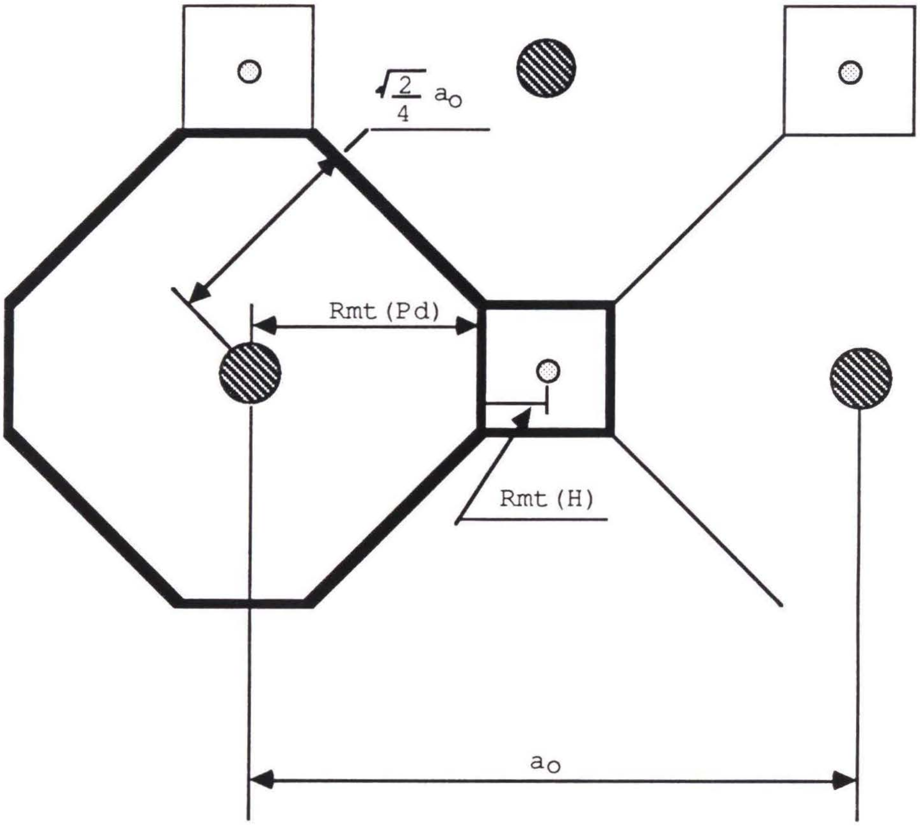

Fig. 6-2. The unit cell of PdH lattice is bounded by the bold lines. It is divided into two sub-cells, each of which contains one atom, Pd or H.

$\sigma_H(\mathbf{r})$ are defined.

The muffin-tin potentials of Pd and H, $v_{Pd}(r)$ and $v_H(r)$, have also been given and arranged as the input data.

The following sections will show the detailed computational procedure for the application of both KKR and QKKR method. All of the calculations were carried on the VAX8800.

6.2 KKR CALCULATION

The computer programs of KKR calculation for complex crystal was built up by Faulkner et al. Fig.6-3 shows the computational procedure.

The major input data are ℓ_{max}, $\mathbf{k}$, $v_{Pd}(r)$ and $v_H(r)$, and the output is the determinant

$$D(E,\mathbf{k}) = \det \begin{bmatrix} \underline{X}^{Pd}(E) + \underline{B}(E,\mathbf{k}) & \underline{M}^{12}(E,\mathbf{k}) \\ \underline{M}^{21}(E,\mathbf{k}) & \underline{X}^{H}(E) + \underline{B}(E,\mathbf{k}) \end{bmatrix} , \tag{6.1}$$

where the matrices $\underline{X}^{Pd}(E)$ and $\underline{X}^{H}(E)$ are diagonal

$$X^{Pd}_{L,L'}(E) = \alpha\cdot\cot\eta^{Pd}_{\ell}(E)\cdot\delta_{LL'} , \tag{6.2a}$$

$$X^{H}_{L,L'}(E) = \alpha\cdot\cot\eta^{H}_{\ell}(E)\cdot\delta_{LL'} , \tag{6.2b}$$

with $\ell = 0,1,\cdots,\ell_{max}$. The energy eigenvalues $E^{\lambda}(\mathbf{k})$, which satisfy

$$D(E^{\lambda}(\mathbf{k}),\mathbf{k}) = 0 , \tag{6.3}$$

are found by carefully checking the sign changes of $D(E,\mathbf{k})$ for different value E with certain $\mathbf{k}$ vector.

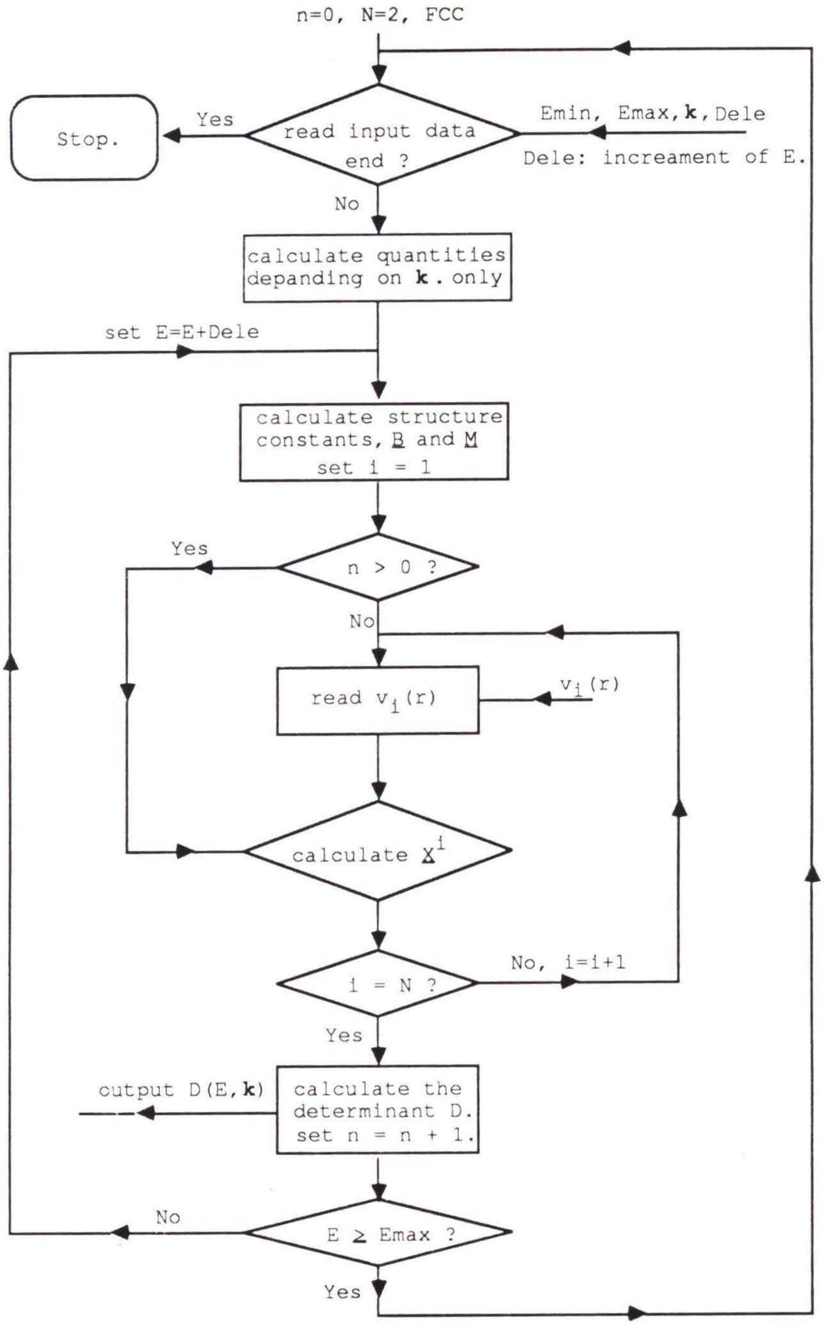

Fig. 6-3. The computational procedure of KKR calculation.

In the calculation, I set $\ell_{max} = 2$. The final results for energy eigenvalues between 0.0 Ry to 1.0 Ry with **k** points along the axis (0,0,1) in reciprocal space have been shown in Fig.6-4. The definition of Ry (i.e. Rydberg), the unit of energy, is defined in Appendix I.

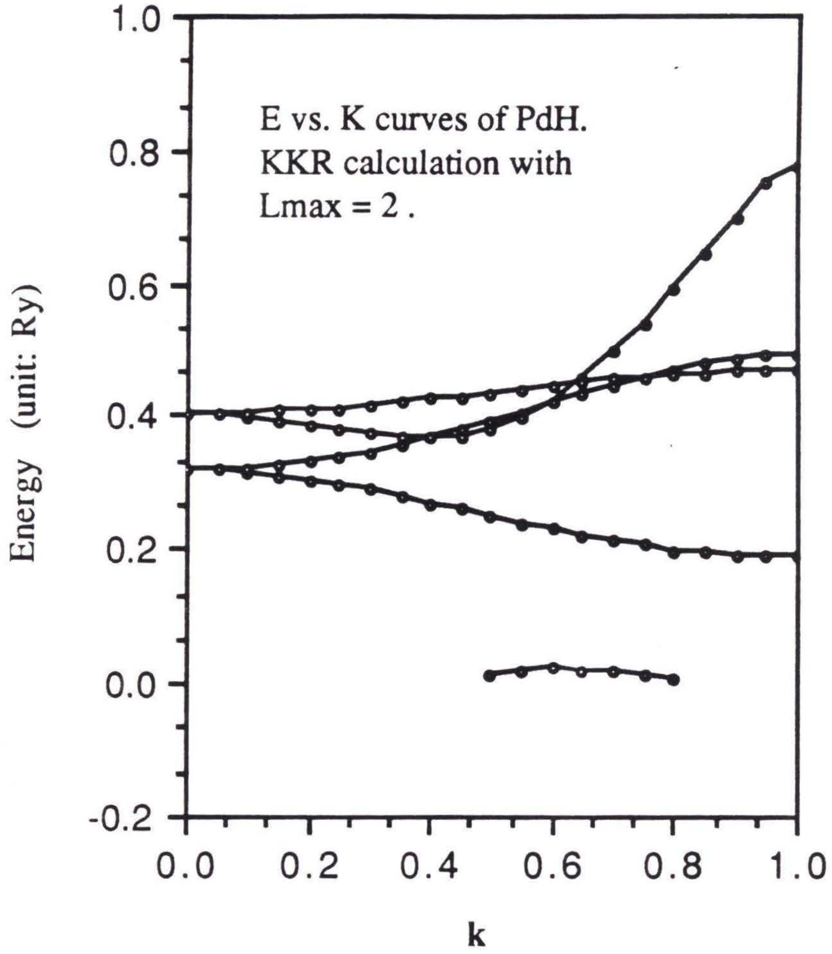

Fig. 6-4. The E vs. **k** curves calculated by KKR method with $\ell_{max} = 2$.

6.3 STEP FUNCTION EXPANSION

Before going through the QKKR calculation, we need to evaluate $\sigma_L(r)$ for both Pd and H sub-cells respectively. In fact, only those L values which relate to $\ell = 0, 4, 6$ and 8 need to be considered, for reasons that will be described in Appendix III. The procedure for the calculation is shown in Fig.6-5. The final results are arranged to be the input data for QKKR calculation.

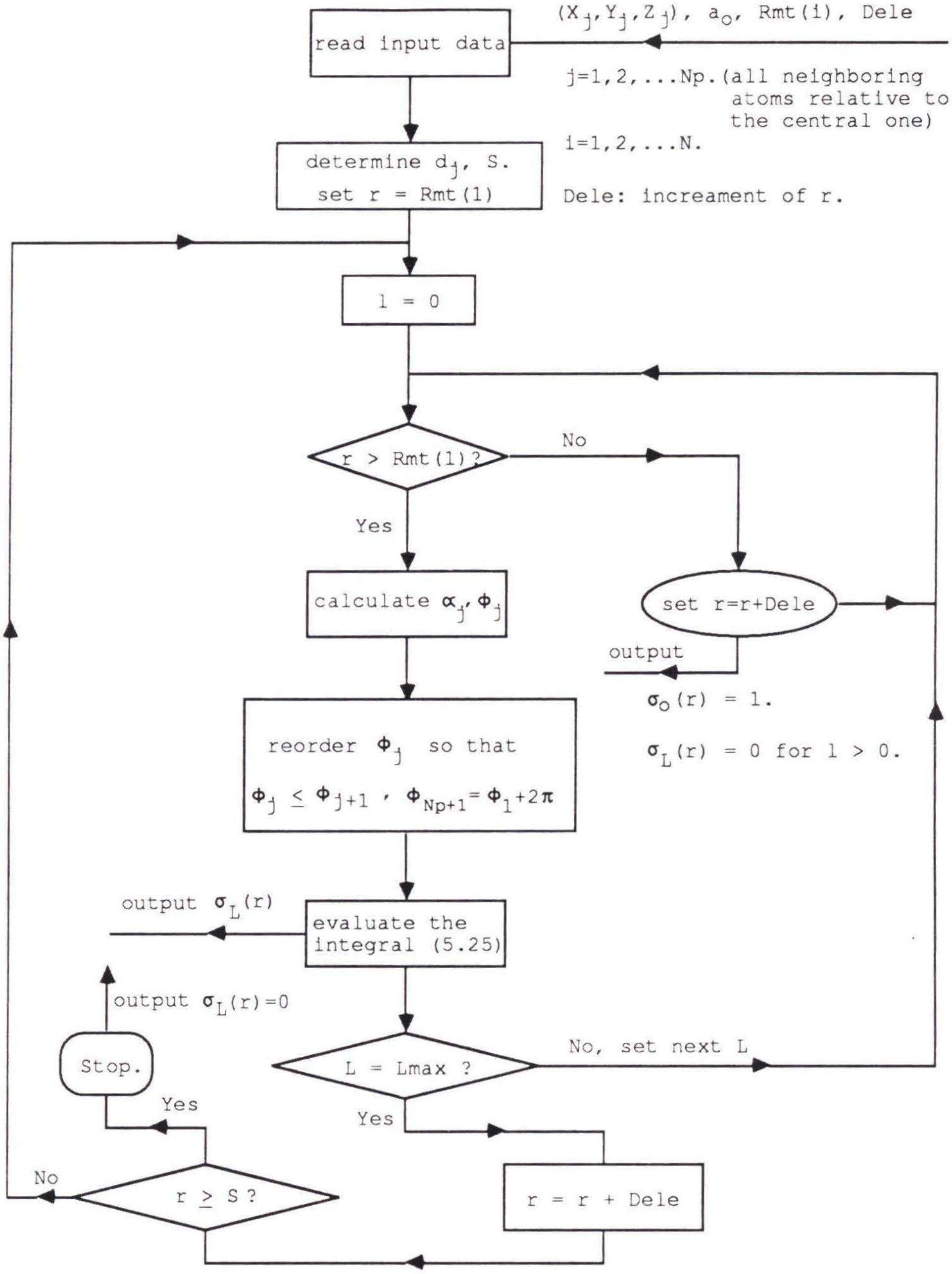

Fig. 6-5. The computational procedure of expanding the step function.

6.4 QKKR CALCULATION

The program for QKKR calculations for complex crystals is developed by combining the KKR program for complex crystals, which I use to calculate the structure constants, and the QKKR program simple crystals, which I use to calculate the sine and cosine matrices. It includes the program for the step functions described in section 5.2. Notice that an important property of QKKR theory is the sine and cosine matrices are nondiagonal, even in the case of muffin-tin potential. This doesn’t mean we have to calculate $(\ell_{max} + 1)^2 \times (\ell_{max} + 1)^2$ elements for each sine or cosine matrix. Using the lattice symmetry property, we can transform the sine and cosine matrices into block diagonal shape so that most elements are zero. The transformation matrix and its related basis functions (other than real spherical harmonics) can be found by applying group theory.

In the case of PdH, the lattice symmetry is described by the point group O_h. The basis functions are called Kubic harmonics represented by $K_L(\mathbf{r})$

$$K_L(\mathbf{r}) = \sum_{L'} U_{LL'} \cdot Y_{L'}(\mathbf{r}) \ , \qquad (6.4)$$

where the transformation coefficients $U_{LL'}$ are given in Appendix III.

Instead of using the real spherical harmonics, we will use the Kubic harmonics in the expansions discussed in chapter 4 and chapter 5. It is easy to prove that the equations still hold, but the Gaunt factors should be written as

$$g^{L}_{L',L''} = \int do \cdot K_L(\mathbf{r}) K_{L'}(\mathbf{r}) K_{L''}(\mathbf{r}) \quad . \tag{6.5}$$

Since the coefficients in $\sigma_L(r)$ were calculated based on the real spherical harmonics, we need to transform them by applying the coefficients $U_{LL'}$ described above. After the sine and cosine expansion matrices are evaluated, we have to transform them back to matrices based on the spherical harmonics in order to be consistent with the structure constant matrices. The computational procedure is shown in Fig.6-6. The results for both $\ell_{max} = 2$ and 4 are given in Fig.6-7.

Since the same input potentials are used for both KKR and QKKR calculations, we expect that the results should be very close. The E vs.**k** curves obtained from both KKR and QKKR methods are combined in Fig.6-8 and Fig.6-9, so that the reader can visualize the comparison of the results.

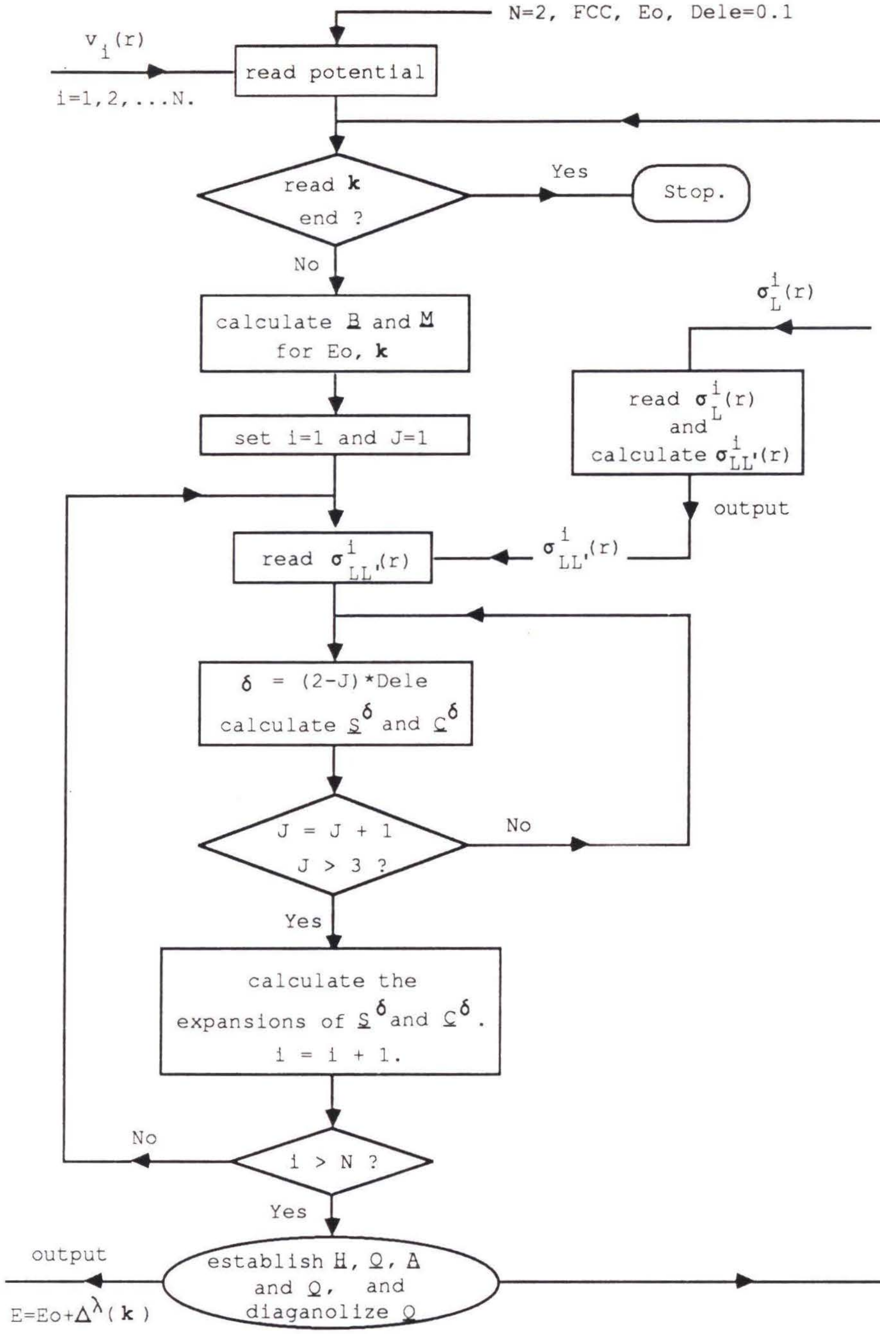

Fig.6-6 The computational procedure of QKKR calculation.

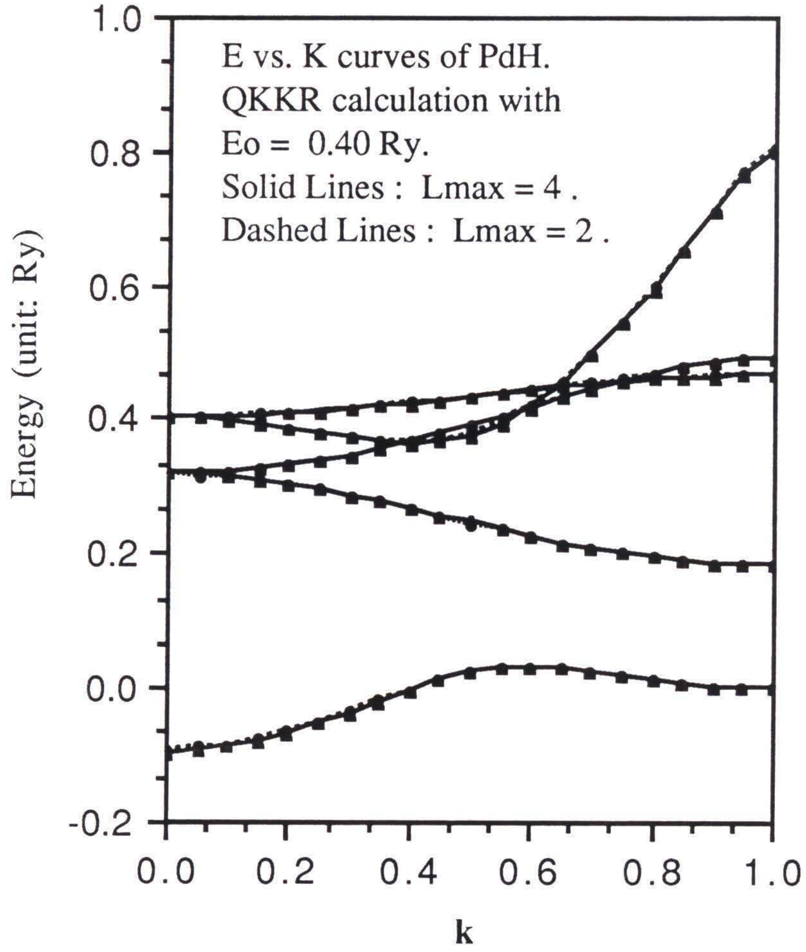

Fig. 6-7. E vs. **k** curves obtained from the QKKR calculations in the both cases of $\ell_{max} = 2$ and $\ell_{max} = 4$ with $E_0 = 0.4$ (Ry) being assumed in the calculation.

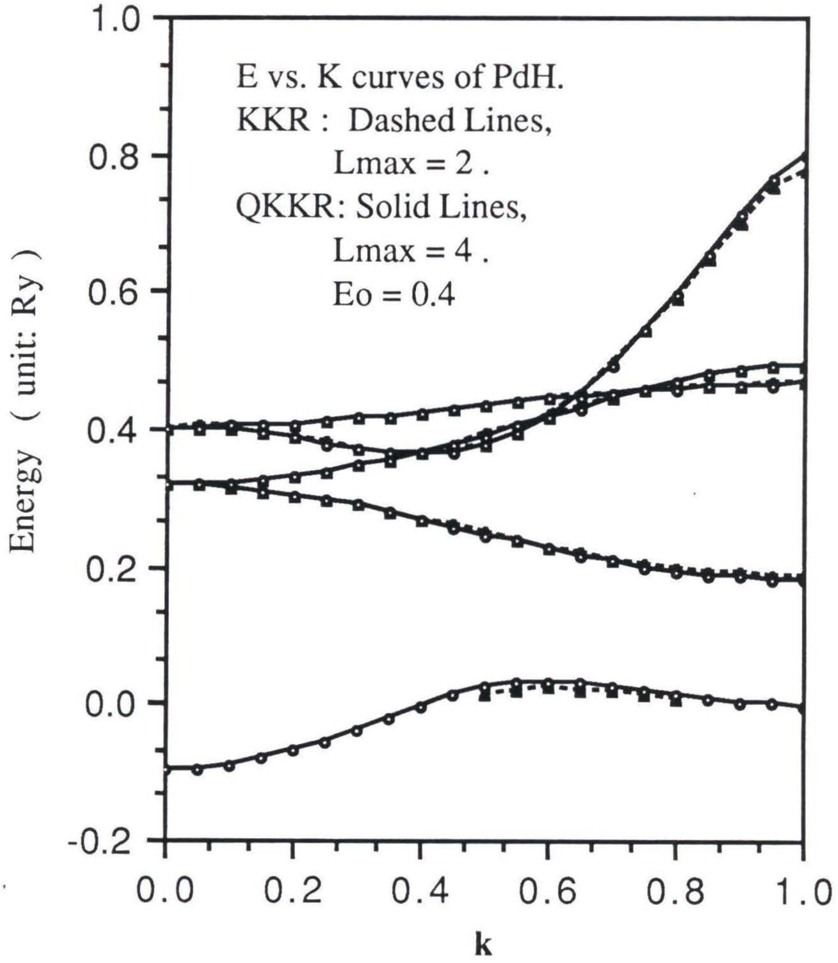

Fig. 6-8. E vs. **k** curves obtained from the KKR and QKKR calculations. $\ell_{max} = 2$ is assumed in the KKR calculation, $\ell_{max} = 4$ with $E_0 = 0.4$ (Ry) is assumed in the QKKR calculation.

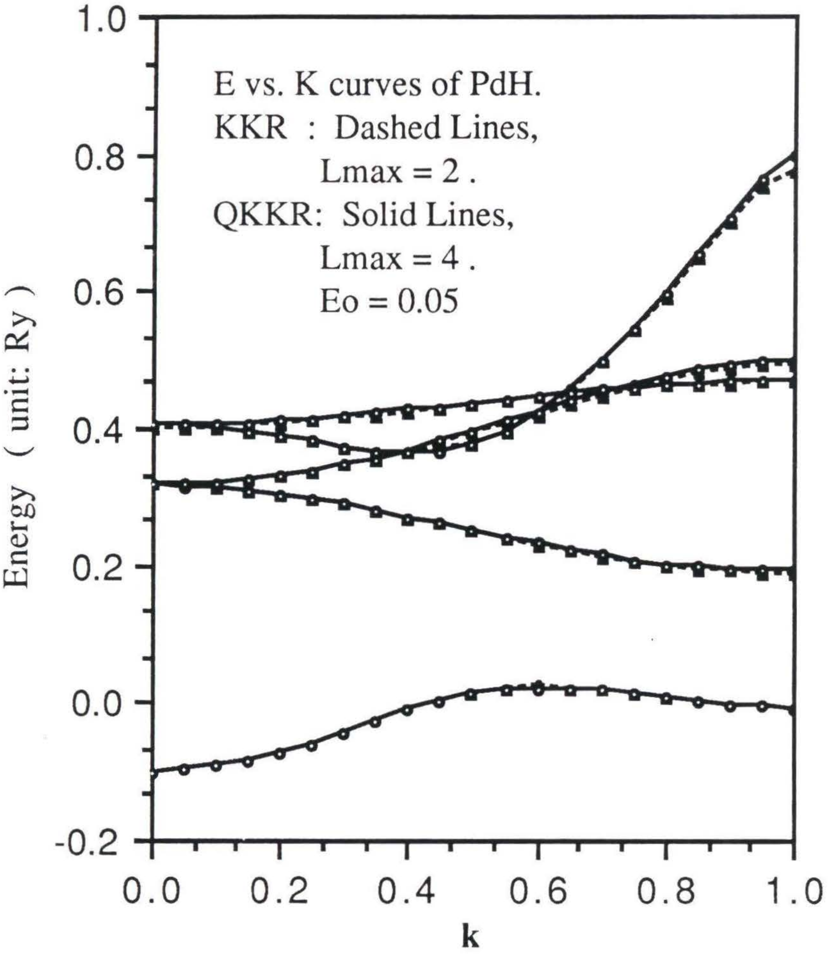

Fig. 6-9. E vs. **k** curves obtained from the KKR and QKKR calculations. $\ell_{max} = 2$ is assumed in the KKR calculation, $\ell_{max} = 4$ with $E_0 = 0.05$ (Ry) is assumed in the QKKR calculation.

CHAPTER 7

CONCLUSIONS

From the E vs. **k** curves shown in the last chapter, we may conclude that:

1. When we choose $E_0 = 0.4$ Ry, which is at about the middle of the bands of interest, the QKKR calculation gives very accurate results within the range of the energy bands.

2. As we expected, the closer to E_0 the energy eigenvalue is, the more accurate it will be.

3. If we change E_0 to 0.05 Ry, our calculations show that the results from the QKKR calculation are almost unchanged. This stability property comes from the fact that the quadratic expansions of sine and cosine matrices in equation (4.19) provide very good approximation over a wide range of energies.

4. The evidence that the difference between the results for $\ell_{max} = 2$ and $\ell_{max} = 4$ in QKKR calculation is very small can be considered, conventionally, as the result of the fast convergence of the QKKR method.

5. In order to evaluate the E vs. **k** data with the KKR

method, I had to not only invest a lot of expensive CPU hours to calculate many determinants but also labor hours to disentangle the degenerate energy eigenvalues related to the multiple zeroes of the determinants. Compared with the KKR method, QKKR calculations save a large amount of time and provide a direct way to achieve self-consistent calculations.

Therefore the application of QKKR calculation for complex crystals works as well as for simple crystals.

Notice that the reason I use muffin-tin potential here is to meet the assumption in ordinary KKR calculations so that the comparisons can be made. Actually, it is not necessary in QKKR calculations to assume that the potential is in the muffin-tin form. This fact implies that the QKKR method will have wider applications than the ordinary KKR.

Since a general method for evaluating the step function has been established, we are able to apply the QKKR method to a wide range of materials, even those with very complicated crystal structures. This is a task in my future work.

APPENDIX I

ATOMIC UNITS

It is well-known that the single electron Schrödinger equation is in the form as

$$[- \frac{\hbar^2}{2Me} \cdot \nabla^2 + V(\mathbf{r})] \cdot \Psi(\mathbf{r}) = E \cdot \Psi(\mathbf{r}) \quad . \qquad (I.1)$$

If we choose the unit of energy as Ry (Rydberg), which is defined as

$$1 \text{ Ry} = \frac{Me \cdot e^4}{2 \cdot \hbar^2} \quad , \qquad (I.2)$$

and the unit of length as Bohr radius, i.e. $\hbar^2/2Me$, it is easy to prove that the Schrödinger equation will become

$$[-\nabla^2 + V(\mathbf{r})] \cdot \Psi(\mathbf{r}) = E \cdot \Psi(\mathbf{r}) \quad . \qquad (I.3)$$

These units are called atomic units.

APPENDIX II

REAL SPHERICAL HARMONICS

In order to avoid using complex functions in computational programming, it is very helpful to introduce the real spherical harmonics other than the normal spherical harmonics in our band theory calculations.

The real spherical harmonics are defined as

$$Y_L(\mathbf{r}) = A_L \cdot P_{\ell}^{|m|}(\cos\theta) \cdot \begin{cases} \cos m\phi & \text{if } m \geq 0 \\ \sin|m|\phi & \text{if } m < 0 \,, \end{cases} \qquad \text{(II.1)}$$

The factors A_L are

$$A_L = \begin{cases} [(2\ell + 1)/4\pi]^{\frac{1}{2}} & \text{if } m = 0 \\ \{[(2\ell + 1) \cdot (\ell - |m|)!/[2\pi(\ell + |m|)!]\}^{\frac{1}{2}} & \text{if } m \neq 0. \end{cases} \qquad \text{(II.2)}$$

APPENDIX III

The Kubic harmonics $K_L(\mathbf{r})$, first introduced by Von der Large and Bethe[24], are defined as the linear combinations of the spherical harmonics:

$$K_L(\mathbf{r}) = \sum_{L'} U_{LL'} \cdot Y_{L'}(\mathbf{r}) \quad , \qquad \text{(III.1)}$$

so that they are the basis functions belonging to a irreducible representation of the cubic group O_h, the elements of which rotate the cubic lattice properly or improperly and leave the lattice invariant. The subscripts L in the equation (III.1) represent the following indexes:

ℓ: the ordinary angular momentum quantum number.

q: type of irreducible representation.

μ: $= 1,2,..,N_q$. N_q is the dimension of the qth irreducible representation.

Those elements of the transformation matrix $\underline{U}$ can found from the work of Altmann and Cracknell[25].

For one-dimensional irreducible representation of the cubic group, it has been shown that[25] the related Kubic harmonics are:

$$K_0(\mathbf{r}) = Y_{0,0}(\mathbf{r}) \ , \tag{III.2a}$$

$$K_4(\mathbf{r}) = 0.76376261 \cdot Y_{4,0}(\mathbf{r}) + 0.64549722 \cdot Y_{4,4}(\mathbf{r}) \ , \tag{III.2b}$$

$$K_6(\mathbf{r}) = 0.35355339 \cdot Y_{6,0}(\mathbf{r}) - 0.93541435 \cdot Y_{6,4}(\mathbf{r}) \ , \tag{III.2c}$$

$$K_8(\mathbf{r}) = 0.71807033 \cdot Y_{8,0}(\mathbf{r}) + 0.38188131 \cdot Y_{8,4}(\mathbf{r}) + 0.58184333 \cdot Y_{8,8}(\mathbf{r}) \ , \tag{III.2d}$$

$$\vdots$$

Truncated at $\ell = 8$, the local potential, wave functions and the step function can be expanded in terms of the Kubic harmonics (in the case of cubic lattice) as the following form:

$$f(\mathbf{r}) = f_0(r) \cdot K_0(\mathbf{r}) + f_4(r) \cdot K_4(\mathbf{r}) + f_6(r) \cdot K_6(\mathbf{r}) + f_8(r) \cdot K_8(\mathbf{r}) \ . \tag{III.3}$$

Therefore, in the expansion of the step function in terms of the real spherical harmonics (see section 6.3), only those (ℓ,m) equaling (0,0), (4,0), (4.4), (6,0), (6,4), (8,0), (8,4) and (8,8) need to be considered.

By applying group theory[26], it can be shown that the sine and cosine matrices will be in the form as displayed in Fig.III-1, for $\ell_{max} = 4$.

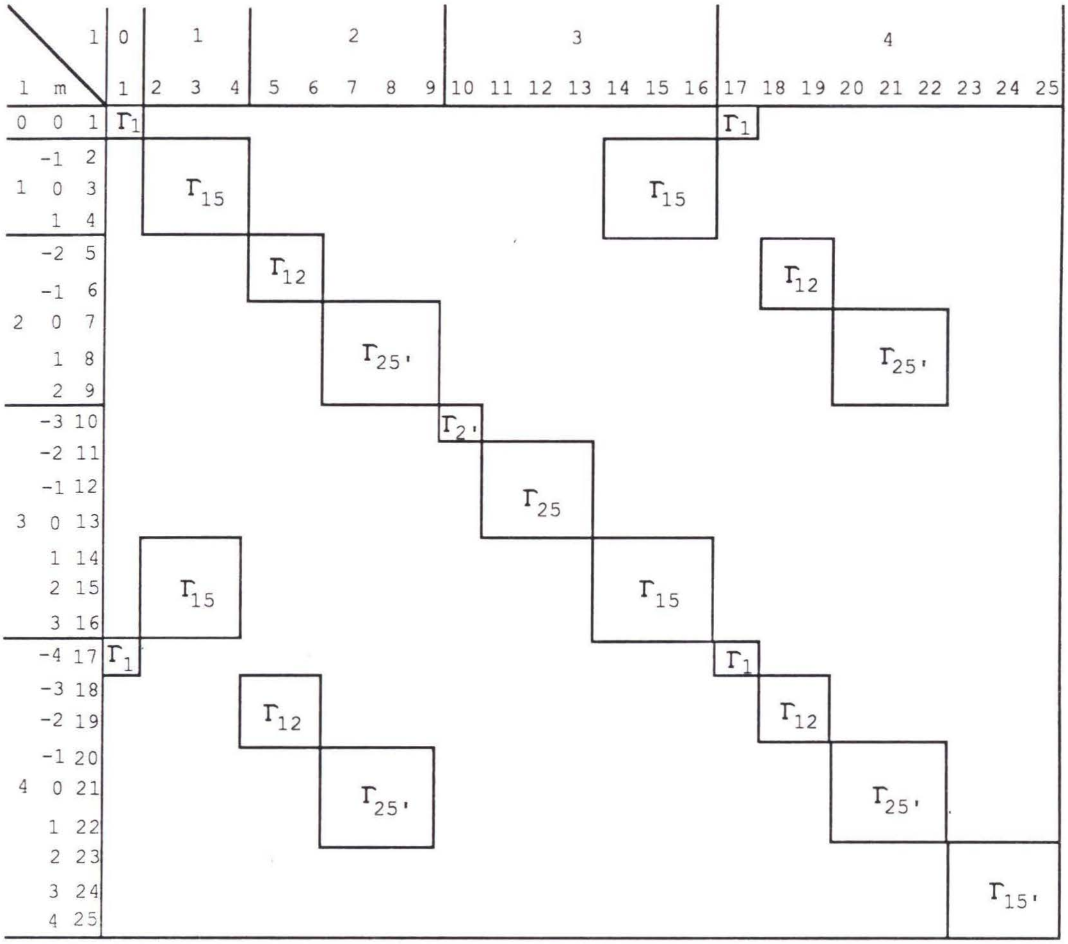

Fig. III-1. The sine or cosine matrix is reduced into block form based on the irreducible representations of cubic group, where $\ell_{\max} = 4$.

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