

9

CHAPTER I



INTRODUCTION

The success in accounting for various properties of solids such as transport or electrical properties, optical properties, magnetic properties and the cohesion of solids depends on detailed knowledge of the components contained in the solids. Many of these properties are directly dependent upon the role of electrons in the solids the elucidation of which relies on quantum mechanics. This indicates the importance of the quantum mechanical description of electron states in solids.

1. What is a band structure?

The electronic properties of solids can be explained by quantum mechanics by taking into account the Coulomb interactions among the nuclei and the electrons of the crystal. Solutions of the general equations for the enormous number of particles ($\sim 10^{23}$ per cm^3) are impossible to obtain, but one can adopt simplified models within the general framework and physically significant results can then be obtained.

It is necessary and a common practice to describe electron states in solids in the adiabatic one-electron approximation which consists of the following steps. First of all one uses the Born-Oppenheimer approximation: the motion of the ion cores and of the electrons are separated in a quantum mechanical treatment of the

entire solid state problem and one assumes that the electrons follow adiabatically the motion of the ion cores. This step of approximation is equivalent to a neglect of phonon-phonon interaction and electron-phonon coupling and it follows that the electronic states are defined by keeping the ion cores in their lattice positions and by considering only the wave functions of the electrons. This approximation leads to a many-electron problem which still cannot be solved. In the next step the independent particle model is then commonly adopted because of its success in atomic and molecular problems. In such a model the electronic wave functions are separated and this yields the total wave function of the system in products of one electron wave functions. Thus Hartree-Fock equations for the electrons of the crystal result. The self-consistent Hartree-Fock equations are still too difficult to solve. Therefore further simplifications must be introduced in order to obtain numerical results. At this step the band approximation is adopted. In such an approximation, a crystal potential $V(\underline{r})$ can be written as the sum of atomic-like potentials at the lattice sites and this potential is the same for all electrons of the crystal. Hence this step leads one to solve only one electron problem.

A fundamental idealization which is often claimed is to restrict attention to the states of a single crystal with a rigid, infinitely and perfectly periodic lattice. For such a perfect crystal the potential is strictly periodic so we have the potential energy of the electron at position \underline{r} in the crystal

$$V(\underline{r}) = V(\underline{r} + \underline{r}_S) \quad \dots 1)$$

with lattice vectors

$$\underline{r}_s = s_1 \underline{\tau}_1 + s_2 \underline{\tau}_2 + s_3 \underline{\tau}_3 \quad \dots 2)$$

spanning the whole lattice. Here s_1 , s_2 , and s_3 are integers, and $\underline{\tau}_1$, $\underline{\tau}_2$, and $\underline{\tau}_3$ are independent primitive translation vectors spanning the primitive cell. Through the repetition of the cell, the whole crystal is built. Since the kinetic energy operator $-\nabla^2$ is even and the potential V is invariant under translation, the Hamiltonian

$$H(\underline{r}) = -\nabla^2 + V(\underline{r}) \quad \dots 3)$$

is translational invariant and because of the abelian property of the group of the lattice translations, the wave function of the electron satisfies Bloch's theorem

$$\Psi_{\underline{k}}(\underline{r} + \underline{r}_s) = \exp(i\underline{k} \cdot \underline{r}_s) \Psi_{\underline{k}}(\underline{r}). \quad \dots 4)$$

For a crystal with infinite extent, we are not interested in surface properties and the wave vector \underline{k} characterizing the transformation behaviour of $\Psi_{\underline{k}}(\underline{r})$ with respect to lattice translations is a good quantum number. The approximations outlined above reduce the many body problem into a one-electron problem

$$H(\underline{r}) \Psi_{\underline{k}}(\underline{r}) = E(\underline{k}) \Psi_{\underline{k}}(\underline{r}). \quad \dots 5)$$

The solutions of this problem form what we call a "band structure". It is the functional dependence of the energy on the wave vector $E(\underline{k})$.

Because of the periodicity of the reciprocal space

$$E(\underline{k}) = E(\underline{k} + \underline{K}_n) \quad \dots 6)$$

for any reciprocal lattice vector \underline{K}_n , the knowledge of the energy spectrum and wave functions in the first Brillouin zone is sufficient to explain the whole crystal in the framework of the one-electron approximation. The things to do in band structure calculations are the determination of all the energy eigenvalues for various \underline{k} in the first Brillouin zone and may be the eigenfunctions satisfying the crystal Schrödinger equation 5).

2. The classification of band structure calculations

The calculations of electronic band structures become a problem of computational technique which is a matter of finding a procedure that works and will generate solutions with desired degree of numerical accuracy for various solids. The band structure theory may be divided into two broad groups. One tries to improve the so-called "first principles" methods in order to obtain quantitative agreement with experiment and the other makes use of experimental data to which the band structure is fitted.

The methods in the former group, which we classify as the first-principles calculations, are those that are performed directly by replacing the crystal potential with atomic or ionic potentials that have been calculated consistently. These methods of solving one electron wave equation consistently include the orthogonalized-

plane-wave, the augmented-plane-wave and the Green's function methods.

The latter group approaches the energy band problem from a purely empirical point of view and constructs an empirical band model which accounts for as much experimental information as possible. The empirical methods for determination of electronic band structures are based upon pseudopotentials, the methods of replacing the crystal potentials through the weak effective potentials that are completely parametrized according to experimental data.

3. Basic concept of pseudopotential methods

The basic feature of the model potential or the pseudopotential methods is the utilization of indirect information about the shapes of the Fermi surface, optical studies and information from the numerous band structure calculations of many simple metals, especially the alkaline ones. From such information we know that band structures of simple metals are nearly free-electron-like and closely resemble the band structure of an electron gas perturbed by a weak periodic potential, even though their actual potentials are very strong. This circumstance has been explained as due to the fact that most of the large negative potential energy of a valence electron has been cancelled against the large positive kinetic energy which the electron has when it is inside the core of an atom. This cancellation gives a weak net effective potential. This is the basic idea of the invention of the pseudopotential techniques

given by various authors ^{1, 2, 3}. The formalism of this theory justifies the simple models for treating valence electrons of simple metals and it provides a new potential, the pseudopotential, which leads to the same band structure as the true potential even though they are usually quite weak. In practice, the pseudopotential may be obtained from first-principles calculations or guessed from experimental measurements on the metal in question. This formalism leads to a particularly simple and compact parametrization of the band structure in the nearly-free-electron case.

However, the pseudopotential theory is not applicable to metals with narrow valence bands such as the noble, transition and actinide metals. For these metals, it is not possible to describe their band structures as a nearly-free-electron one. Nevertheless, ⁴ it has been shown independently by Hodges et al. and by

¹ J.C. Phillips and L. Kleinman, "New Method for Calculating Wave Functions in Crystals and Molecules," Physical Review B, 116, 287-294 (1959).

² H. Cohen and V. Heine, "Cancellation of Kinetic and Potential Energy in Atoms, Molecules and Solids," Physical Review B, 122, 1821-1826 (1961).

³ B.J. Austin, V. Heine and L.J. Sham, "General Theory of Pseudopotentials," Physical Review B, 127, 276-282 (1962).

⁴ L. Hodges, H. Ehrenreich and N.D. Lang, "Interpolation Scheme for Band Structure of Noble and Transition Metals: Ferromagnetism and Neutron Diffraction in Ni," Physical Review B, 152, 505-526 (1966).

5, 5a
 Mueller that these pseudopotential techniques can be extended to the transition metals. At least in the case of copper, the band structure can be characterized by ascribing a free electron like behaviour to the conduction bands, in a manner similar to that suggested by Harrison⁶ as appropriate for Al, and a tight binding behaviour to the d-bands as suggested by Fletcher⁷. The hybridization between these two sets of bands was included in a semi-empirical fashion by introducing k-dependent functions. By expressing the momentum matrix elements and the overlap and hybridization integrals in terms of adjustable parameters, it was possible to reproduce first principles calculations with great accuracy using very little computer time. The number of parameters that need fitting is reasonably large (about fifteen parameters), but they can be obtained easily by fitting eigenvalues to experiment at points of high symmetry in the Brillouin zone where the secular determinant has a very simple form.

⁵ F.M. Mueller, "Combined Interpolation Scheme for Transition and Noble Metals," Physical Review B, 153, 659-669 (1967).

^{5a} Samphao Jongjitta, "Interpolation Schemes for Transition Metal Band Structures." Unpublished Master's Thesis, Department of Physics, Chulalongkorn University (1976).

⁶ W.A. Harrison, "Band Structure of Aluminum," Physical Review B, 118, 1182-1189 (1960).

⁷ G.C. Fletcher, "Density of States Curve for the 3d Electrons in Nickel," Proceeding of the Physical Society of London, A65, 192-202 (1952).

This procedure provides a method of interpolating between energy eigenvalues calculated at points of high symmetry in the Brillouin zone and in that way one obtains electron dispersion relations that are valid for all \underline{k} in the Brillouin zone.

In the following section, the simplest example of interpolation schemes for calculations of the energy bands of transition metals will be introduced in order to provide some background for readers who are not active in this area as well as to provide the basic understanding necessary for the subsequent discussions.

4. Description of the interpolation scheme for transition metal

For the simplest case, we shall present a scheme for paramagnetic transition metals so that spin functions can be neglected. We set up here the formal development of the empirically devised scheme of Hodges et al.⁴ for monatomic face-centered-cubic(fcc) metal.

The interpolation scheme for transition metals is based on the following ideas. From first-principles calculations, one knows that except for important hybridization effects the d-bands closely resemble those obtained in the tight binding approximation whereas the conduction bands are similar to those of nearly free electron calculations. Consequently, the unhybridized d-bands can be represented in terms of linear combinations of atomic orbitals (LCAO) and the lowest conduction bands in terms of a "four-OPW approximation"⁶.

4.a) The model Hamiltonian

The main problem is to solve the eigenvalue equation

$$H B_{\underline{k}n}(\underline{r}) = E_n(\underline{k}) B_{\underline{k}n}(\underline{r}) \quad \dots 7)$$

where $B_{\underline{k}n}(\underline{r})$ are the Bloch eigenfunctions, \underline{k} labels the wave vector and n labels the band index. $B_{\underline{k}n}(\underline{r})$ can be written as linear combinations of five LCAO's $b_{\underline{k}\mu}$ (indexed by $\mu = 1, 2, \dots, 5$) and four OPW's $b_{\underline{k}K}(\underline{r})$ (indexed by $\underline{K} = \underline{K}_1, \underline{K}_2, \underline{K}_3, \underline{K}_4$):

$$B_{\underline{k}n}(\underline{r}) = \sum_{\mu} a_{n\mu}(\underline{k}) b_{\underline{k}\mu} + \sum_{\underline{K}} a_{n\underline{K}}(\underline{k}) b_{\underline{k}\underline{K}} \quad \dots 8)$$

The LCAO's representing 3d-bands in tight binding approximation correspond to the five basis states ϕ_{μ} of the 3d-orbitals which are taken to be proportional to xy , yz , zx , $\frac{1}{2}(x^2 - y^2)$ and $\frac{1}{2}(1/\sqrt{3})(3z^2 - r^2)$, the basis functions for irreducible representations of the cubic point group. They are defined by

$$\langle \underline{r} | \underline{k} \mu \rangle = b_{\underline{k}\mu} = N^{-1/2} \sum_{\underline{R}_1} \exp(i\underline{k} \cdot \underline{R}_1) \phi_{\mu}(\underline{r} - \underline{R}_1), \quad \dots 9)$$

$(\mu = 1, 2, \dots, 5)$

where $\phi_{\mu}(\underline{r} - \underline{R}_1)$ are atomic 3d-orbitals centered at the lattice sites \underline{R}_1 and N is the number of atoms in solid. The atomic orbitals ϕ_{μ} have the form

$$\begin{aligned} \phi_1(\underline{r}) &= (15/4\pi)^{1/2} xy \cdot f^{T_{2g}}(r)/r^2, \\ \phi_2(\underline{r}) &= (15/4\pi)^{1/2} yz \cdot f^{T_{2g}}(r)/r^2, \\ \phi_3(\underline{r}) &= (15/4\pi)^{1/2} zx \cdot f^{T_{2g}}(r)/r^2, \quad \dots 10) \\ \phi_4(\underline{r}) &= (15/16\pi)^{1/2} (x^2 - y^2) \cdot f^{E_g}(r)/r^2, \\ \phi_5(\underline{r}) &= (5/16\pi)^{1/2} (3z^2 - r^2) \cdot f^{E_g}(r)/r^2 \end{aligned}$$

and satisfy $[P^2/2m + U(r)] \phi_\mu(\underline{r}) = E_{\text{atomic}} \phi_\mu(\underline{r})$ where $U(r)$ is the atomic potential and $f^\mu(r)$ are the normalized radial functions of the isolated atom:

$$\int_0^\infty [r f^\mu(r)]^2 dr = 1.$$

8

Following Slater and Koster⁸, the nonorthogonality of the atomic orbitals associated with different sites is assumed.

The appropriate OPW's for $1/4^{\text{th}}$ of the Brillouin zone in which $k_y \geq k_x \geq k_z \geq 0$ (see Fig. 1) are formed from only four OPW's $\langle \underline{r} | \underline{k} + \underline{K} \rangle$ where $\underline{K}_1 = (\pi/4a) \cdot (0, 0, 0)$, $\underline{K}_2 = (\pi/4a) \cdot (0, \bar{16}, 0)$, $\underline{K}_3 = (\pi/4a) \cdot (\bar{8}, \bar{8}, \bar{8})$ and $\underline{K}_4 = (\pi/4a) \cdot (\bar{8}, \bar{8}, 8)$, since these suffice

8

J.C. Slater, and G.F. Koster, "Simplified LCAO Method for the Periodic Potential Problem," Physical Review B, 94, 1498-1524(1954).

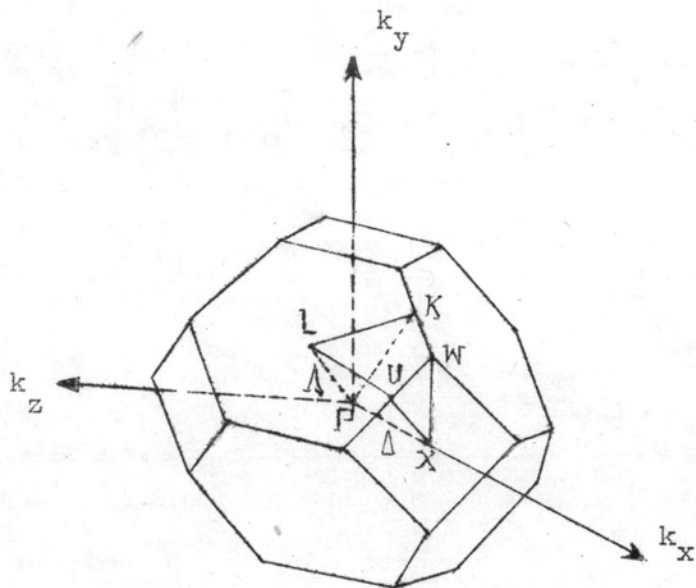


Fig. 1 The Brillouin zone of the fcc lattice showing the $1/48$ primitive wedge used in the calculations, with lines and points of high symmetry.

to form the symmetrized linear combinations of OPW's that are the lowest empty lattice eigenfunctions. This choice makes our basis fully orthogonal. The OPW's have the form

$$\begin{aligned} \langle \underline{r} | \underline{k} + \underline{K}, d \rangle &= b_{\underline{k}\underline{K}}(\underline{r}), \\ &= \mathcal{N}_{\underline{k}\underline{K}}^{-1/2} \left[\langle \underline{r} | \underline{k} + \underline{K} \rangle - \sum_{\underline{C}} \langle \underline{r} | \underline{k}\underline{C} \rangle \langle \underline{k}\underline{C} | \underline{k} + \underline{K} \rangle \right] \dots 11) \end{aligned}$$

where the \underline{K} are reciprocal lattice vectors and the normalization factor is given by

$$\mathcal{N}_{\underline{k}\underline{K}} = 1 - \sum_{\underline{C}} |\langle \underline{k}\underline{C} | \underline{k} + \underline{K} \rangle|^2. \quad \dots 12)$$



The wave functions

$$\langle \underline{r} | \underline{k} + \underline{K} \rangle = (Nv_a)^{1/2} \exp[i(\underline{k} + \underline{K}) \cdot \underline{r}] \quad \dots 13)$$

are plane waves, and v_a is the volume of the unit cell. The index \mathcal{C} runs over all 1s, 2s, ..., 3d states, so the OPW's are orthogonalized to all the core and 3d states.

If we write

$$\langle \underline{r} | \underline{k} \mathcal{C}' \rangle = b_{\underline{k} \mathcal{C}'} \quad \dots 14)$$

where the index \mathcal{C}' includes the LCAO and OPW indices, \mathcal{A} and \underline{K} , the energy eigenvalues are given by the solution of the secular equation

$$\det \left| \langle \underline{k} \mathcal{C}' | H | \underline{k} \mathcal{C}'' \rangle - E \langle \underline{k} \mathcal{C}' | \underline{k} \mathcal{C}'' \rangle \right| = 0 \quad \dots 15)$$

Assuming that all the basis functions 14) form an orthonormal set, that is the nonorthogonality of the basis functions is neglected, the secular equation becomes simply

$$\det \left| \langle \underline{k} \mathcal{C}' | H | \underline{k} \mathcal{C}'' \rangle - E(\underline{k}) \delta_{\mathcal{C}' \mathcal{C}''} \right| = 0 \quad \dots 16)$$

Applying these basis functions, the 9x9 model Hamiltonian will have the block form

$$H_{\text{band}} = \begin{array}{c} 4 \qquad \qquad \qquad 5 \\ \left[\begin{array}{c|c} \text{OPW-OPW} & \text{OPW-LCAO} \\ \hline (\text{OPW-LCAO})^+ & \text{LCAO-LCAO} \end{array} \right] \dots 17) \end{array}$$

In this scheme the matrix elements are represented in parametrized form which is treated below.

4.b) LCAO-LCAO block

To obtain the LCAO-LCAO matrix elements, we use the tight-binding approximation in the manner suggested by Slater and Koster.⁸ The matrix elements $H^{\mu\mu'}$ corresponding to d-d or LCAO-LCAO block are given by

$$H^{\mu\mu'}(\underline{k}) = \langle \underline{k}, \mu | \underline{p}^2/2m + V(\underline{r}) | \underline{k}, \mu' \rangle \quad \dots 18)$$

where the crystal potential $V(\underline{r})$ may be written as a superposition of atomic potentials centered about lattice sites \underline{R}_1 :

$$V(\underline{r}) = \sum_1 U(\underline{r}-\underline{R}_1), \quad \dots 19)$$

as shown schematically in Fig. 2.

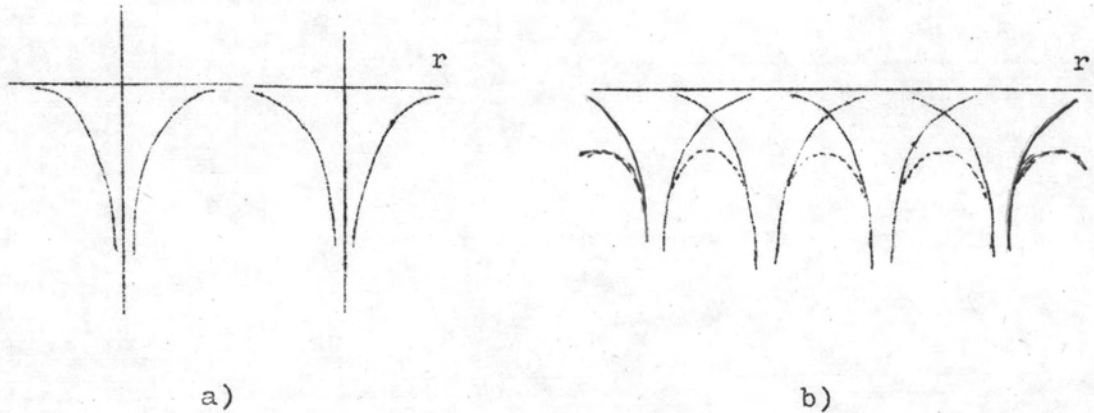


Fig. 2 Showing the construction of the crystal potential b) (broken line) by superposing the atomic potentials a) (dark line) located at various sites.

Using eq. 9) we obtain

$$\begin{aligned}
 H_{\text{band}}^{\mu\mu}(\underline{k}) &= \int N^{-1/2} \sum_{\underline{1}} \exp(-i\underline{k}\cdot\underline{R}_1) \phi_{\mu}^*(\underline{r}-\underline{R}_1) \left[\underline{p}^2/2m + V(\underline{r}) \right] \\
 &\quad \cdot N^{-1/2} \sum_{\underline{1}'} \exp(i\underline{k}\cdot\underline{R}_1) \phi_{\mu'}(\underline{r}-\underline{R}_1) d\underline{r}, \\
 &= N^{-1} \sum_{\underline{1}} \sum_{\underline{1}'} \exp(-i\underline{k}\cdot\underline{R}_1) \\
 &\quad \cdot \int \phi_{\mu}^*(\underline{r}-\underline{R}_1) \left[\underline{p}^2/2m + V(\underline{r}) \right] \phi_{\mu'}(\underline{r}) d\underline{r}, \\
 &= \sum_{\underline{1}} \exp(-i\underline{k}\cdot\underline{R}_1) \left[\int \phi_{\mu}^*(\underline{r}-\underline{R}_1) \left\{ \underline{p}^2/2m + U(\underline{r}) \right\} \phi_{\mu'}(\underline{r}) d\underline{r} \right. \\
 &\quad \left. + \int \phi_{\mu}^*(\underline{r}-\underline{R}_1) \left\{ V(\underline{r}) - U(\underline{r}) \right\} \phi_{\mu'}(\underline{r}) d\underline{r} \right], \\
 &= \left[E_0 + \Delta (\delta_{\mu 4} + \delta_{\mu 5}) \right] \delta_{\mu\mu'} + \sum_{\underline{1} \neq \underline{0}} \exp(-i\underline{k}\cdot\underline{R}_1) \\
 &\quad \cdot \int \phi_{\mu}^*(\underline{r}-\underline{R}_1) \left[V(\underline{r}) - U(\underline{r}) \right] \phi_{\mu'}(\underline{r}) d\underline{r} \\
 &\quad \dots 20)
 \end{aligned}$$

where $\int \phi_{\mu}^*(\underline{r}) \left[\underline{p}^2/2m + U(\underline{r}) \right] \phi_{\mu}(\underline{r}) = E_0$ for $\mu = 1, 2, 3$

(the orbitals belonging to the irreducible representation T_{2g})

and $E_0 + \Delta$ for $\mu = 4, 5$ (the orbitals belonging to the irreducible representation E_g). Δ corresponds to the crystal field splitting

at point Γ (the center of symmetry (0,0,0)).

Retaining only the nearest neighbour interaction, the matrix elements $H^{\mu\mu'}$ can be expressed in terms of six independent integrals A_1, A_2, \dots, A_6 having the form

$$A_1 = - \int \phi_1^*(x-\frac{1}{2}a, y-\frac{1}{2}a, z) (V-U) \phi_1(x, y, z) dx dy dz, \text{ etc.}$$

Instead of computing these integrals analytically we obtain them as adjustable parameters as in the LCAO interpolation scheme of Slater and Koster⁸ so that the present method agrees with the accurate calculations at high symmetry points in the Brillouin zone for which these calculations have been made. Then these constants are used for making calculations throughout the Brillouin zone. In addition E_0 and Δ are assumed to be adjustable.

To summarize for this block, $E_0, \Delta, A_1, \dots, A_6$ are taken as adjustable parameters to be fitted to the first-principles calculations at high symmetry points. The matrix elements $H^{\mu\mu'}$ can then be calculated throughout the Brillouin zone by making use of those parameters.

4.c) OPW-OPW block

The matrix elements $H^{\underline{K}\underline{K}'}(\underline{k})$ of the OPW-OPW block or s-s block are obtained by making use of the expressions 11) and 13). In the scheme of Hodges et al. the basis states of this block are approximated by plane waves and the orthogonality effects are included through parameters. The plane waves $\underline{k}+\underline{K}_i$ of eq. 13) labelled by

\underline{k}_i for $i = 1, 2, 3, 4$ are used instead of eq. 11) to obtain the diagonal terms as

$$\begin{aligned}
 \langle \underline{k} + \underline{k}_i | H_{\text{band}} | \underline{k} + \underline{k}_i \rangle &= (Nv_a)^{-1/2} \int \exp \{ -i(\underline{k} + \underline{k}_i) \cdot \underline{r} \} \left[\underline{p}^2 / 2m + V(\underline{r}) \right] \\
 &\quad \cdot (Nv_a)^{-1/2} \exp \{ i(\underline{k} + \underline{k}_i) \cdot \underline{r} \} d\underline{r}, \\
 &= (\hbar^2 / 2m) | \underline{k} + \underline{k}_i |^2 + (Nv_a)^{-1} \int \exp \{ -i(\underline{k} + \underline{k}_i) \cdot \underline{r} \} \\
 &\quad \cdot \sum_{\underline{K}'} v_{\underline{K}'} \exp(i\underline{K}' \cdot \underline{r}) \cdot \exp \{ i(\underline{k} + \underline{k}_i) \cdot \underline{r} \} d\underline{r}, \\
 &= (\hbar^2 / 2m) | \underline{k} + \underline{k}_i |^2 + (Nv_a)^{-1} \sum_{\underline{K}'} v_{\underline{K}'} \int \exp(i\underline{K}' \cdot \underline{r}) d\underline{r}, \\
 &= (\hbar^2 / 2m) | \underline{k} + \underline{k}_i |^2 + \sum_{\underline{K}'} v_{\underline{K}'} \delta(\underline{K}'), \\
 &= (\hbar^2 / 2m) | \underline{k} + \underline{k}_i |^2 + V(0) \quad \dots 21)
 \end{aligned}$$

where the crystal potential $V(\underline{r})$ is replaced by its Fourier transformation $\sum_{\underline{K}} v_{\underline{K}} \exp(i\underline{K} \cdot \underline{r})$. $V(0)$ is the Fourier component of the crystal potential with $\underline{K} = (0, 0, 0)$. In this scheme these matrix elements are put into the form

$$\langle \underline{k} + \underline{k}_i | H | \underline{k} + \underline{k}_i \rangle = \beta + \alpha | \underline{k} + \underline{k}_i |^2, \quad \dots 22)$$

hence the diagonal matrix elements give a band of simple parabolic

form as that obtained in the free electron case where β is a constant fixing the zero of energy and α is an adjustable parameter which includes the orthogonalization effects partially.

For nondiagonal matrix elements, $i \neq j$, we have

$$\begin{aligned}
 \langle \underline{k} + \underline{K}_i | H_{\text{band}} | \underline{k} + \underline{K}_j \rangle &= (Nv_a)^{-1/2} \int \exp\{-i(\underline{k} + \underline{K}_i) \cdot \underline{r}\} \left[\frac{\underline{p}^2}{2m} + V(\underline{r}) \right] \\
 &\quad \cdot (Nv_a)^{-1/2} \exp\{i(\underline{k} + \underline{K}_j) \cdot \underline{r}\} d\underline{r}, \\
 &= (\hbar^2/2m) |\underline{k} + \underline{K}_j|^2 (Nv_a)^{-1} \int \exp\{i(\underline{K}_j - \underline{K}_i) \cdot \underline{r}\} d\underline{r} \\
 &\quad + (Nv_a)^{-1} \sum_{\underline{K}} V_{\underline{K}} \int \exp\left[i\left\{\underline{K} - (\underline{K}_i - \underline{K}_j)\right\} \cdot \underline{r}\right] d\underline{r}, \\
 &= 0 + \sum_{\underline{K}} V_{\underline{K}} \delta\left[\underline{K} - (\underline{K}_i - \underline{K}_j)\right]; \quad i \neq j, \\
 &= V_{\underline{K}_i - \underline{K}_j}. \quad \dots 23)
 \end{aligned}$$

Thus the matrix elements of OPW-OPW block can be written in the form

$$H_{\underline{k} + \underline{K}_i, \underline{k} + \underline{K}_j} = \left[\beta + \alpha |\underline{k} + \underline{K}_i|^2 \right] \delta_{ij} + V_{\underline{K}_i - \underline{K}_j} (1 - \delta_{ij}). \quad \dots 24)$$

The off diagonal matrix elements $H_{\underline{k} + \underline{K}_i, \underline{k} + \underline{K}_j}$ involve only two Fourier coefficients, V_{111} and V_{200} , which are also adjusted empirically. According to this scheme the OPW-OPW matrix reads

$$\begin{bmatrix}
 \beta + \alpha |\underline{k} + \underline{K}_1|^2 & V_{200} F_2 & V_{111} F_3 & V_{111} F_4 \\
 V_{200} F_2 & \beta + \alpha |\underline{k} + \underline{K}_2|^2 & V_{111} F_2 F_3 & V_{111} F_2 F_4 \\
 V_{111} F_3 & V_{111} F_2 F_3 & \beta + \alpha |\underline{k} + \underline{K}_3|^2 & V_{200} F_3 F_4 \\
 V_{111} F_4 & V_{111} F_2 F_4 & V_{200} F_3 F_4 & \beta + \alpha |\underline{k} + \underline{K}_4|^2
 \end{bmatrix} \dots 25)$$

The factors F appearing in eq. 25) are the so-called "symmetrizing factors". They have been introduced in practice in order to ensure the occurrence of properly symmetrized linear combinations of OPW's along the symmetry directions and at symmetry points. They are chosen to have the value 1 or 0 at symmetry points according to whether or not the corresponding plane wave is present in the symmetrized combinations of plane waves having the lowest empty lattice energy eigenvalue at that point. The omission of these factors would result in small but undesirable energy splitting and shifts.

4.d) OPW-LCAO block

The off diagonal matrix OPW-LCAO has elements of the form

$$H_{\text{band}}^{\underline{K}\mu}(\underline{k}) = \int b_{\underline{k}\underline{K}}^*(\underline{r}) \left[\underline{p}^2/2m + V(\underline{r}) \right] b_{\underline{k}\mu}(\underline{r}) d\underline{r}. \quad \dots 26)$$

If we approximate the OPW's by their plane wave parts, i.e. we neglect the explicit orthogonalization terms, we obtain

$$\begin{aligned}
H_{\text{band}}^{\underline{K}\mu}(\underline{k}) &= (Nv_a)^{-1/2} \int \exp\{-i(\underline{k}+\underline{K})\cdot\underline{r}\} \left[\underline{p}^2/2m + V(\underline{r}) \right] \\
&\quad \cdot N^{-1/2} \sum_{\underline{l}} \exp(i\underline{k}\cdot\underline{R}_l) \phi_{\mu}(\underline{r}-\underline{R}_l) d\underline{r}, \\
&= v_a^{-1/2} \int \exp\{-i(\underline{k}+\underline{K})\cdot\underline{r}\} \left[\underline{p}^2/2m + U(\underline{r}) \right] \phi_{\mu}(\underline{r}) d\underline{r} \\
&\quad + v_a^{-1/2} \int \exp\{-i(\underline{k}+\underline{K})\cdot\underline{r}\} \left[V(\underline{r}) - U(\underline{r}) \right] \phi_{\mu}(\underline{r}) d\underline{r}, \\
&= E_{\text{atomic}} \cdot v_a^{-1/2} \int \exp\{-i(\underline{k}+\underline{K})\cdot\underline{r}\} \phi_{\mu}(\underline{r}) d\underline{r} \\
&\quad + \bar{U} \cdot v_a^{-1/2} \int \exp\{-i(\underline{k}+\underline{K})\cdot\underline{r}\} \phi_{\mu}(\underline{r}) d\underline{r}, \\
&= (E_{\text{atomic}} + \bar{U}) v_a^{-1/2} \int \exp\{-i(\underline{k}+\underline{K})\cdot\underline{r}\} \phi_{\mu}(\underline{r}) d\underline{r}. \quad \dots 27)
\end{aligned}$$

This expression is adopted by assuming that the term $V(\underline{r})-U(\underline{r})$ or $\sum_{\underline{l} \neq 0} U(\underline{r}-\underline{R}_l)$ is relatively slow-varying and it is approximated by

a constant \bar{U} . By expanding the exponential factor appearing in 27) in spherical harmonics and spherical Bessel functions and noting that only the term $l = 2$ contributes to eq. 27), i.e.

$$4\pi \sum_{m=-2}^2 (-i)^2 j_2(|\underline{k}+\underline{K}|r) Y_{2m}^*(\hat{r}) Y_{2m}(\widehat{\underline{k}+\underline{K}}), \quad \dots 28)$$

the radial part of eq. 27) may be reduced to the parametrized form

$$\int j_2(|\underline{k}+\underline{K}|r) f^{\mu}(r) r^2 dr \propto j_2(|\underline{k}+\underline{K}|B_1) \quad \dots 29)$$

where the integral has been evaluated on the assumption that $r^2 f^\mu(r)$ is strongly peaked at B_1 . The constant factors proportional to $(E_{\text{atomic}} + \bar{U})$ may be combined into other adjustable parameters B_2 and B_3 (for the T_{2g} and E_g orbitals, respectively, since the \bar{U} may not be applicable to both types of orbitals). Again the symmetrizing factors F have been introduced for the same reasons explained in 4.c) to give the final parametrized result

$$H_{\text{band}}^{Ki}(\underline{k}) = B_2 j_2(|\underline{k}+\underline{K}|B_1) \left[\frac{(\underline{k}+\underline{K})_\mu (\underline{k}+\underline{K})_\nu}{|\underline{k}+\underline{K}|^2} \right] F_{\underline{K}}(\underline{k}),$$

where $(i, \mu, \nu) = (1, x, y), (2, y, z), (3, z, x);$

$$H_{\text{band}}^{K4}(\underline{k}) = B_3 j_2(|\underline{k}+\underline{K}|B_1) \left[\frac{(\underline{k}+\underline{K})_x^2 - (\underline{k}+\underline{K})_y^2}{2|\underline{k}+\underline{K}|^2} \right] F_{\underline{K}}(\underline{k}), \quad \dots 30)$$

$$H_{\text{band}}^{K5}(\underline{k}) = B_3 j_2(|\underline{k}+\underline{K}|B_1) \sqrt{\frac{3}{6}} \left[\frac{3(\underline{k}+\underline{K})_z^2}{|\underline{k}+\underline{K}|^2} - 1 \right] F_{\underline{K}}(\underline{k}).$$

These equations are a drastically approximated version of the original equations 27).

To summarize, there are 15 parameters appearing in this scheme to be fitted: $E_0, \Delta, A_1, A_2, A_3, A_4, A_5, A_6, \beta, \alpha, V_{111}, V_{200}, B_1, B_2, B_3$. These are chosen by fitting the pseudo-potential bands at high symmetry points to those accurately calculated from first-principles. We have now completed the description of this scheme.

The success of the interpolation scheme of Hodges et al.⁴ as given above, and that of Mueller⁵, in being able to parametrize band structures of transition metals obtained from first-principles calculations, leads one to enquire whether it might be possible to justify these schemes from first-principles just as the nearly free electron scheme is justified in simpler cases by pseudopotential theory. In order to understand the nature of the model Hamiltonians underlying such schemes, Heine⁹ has derived these Hamiltonians from first principles by exhibiting them as a transformation of the fundamental Korringa-Kohn-Rostoker formulation of the energy band problem. This derivation is quite heuristic but physical motivated. The subsequent derivations of interpolation schemes from first principles by various authors such as Hubbard^{10, 11}, Jacobs¹²,

⁹ V. Heine, "s-d Interaction in Transition Metals," Physical Review B, 153, 673-682(1967).

¹⁰ J. Hubbard, "The Approximate calculation of Electronic Band Structure," Proceeding of the Physical Society of London, 92, 921-937(1967).

¹¹ J. Hubbard and N.W. Dalton, "The Approximate Calculation of Electronic Band Structures II Application to Copper and Iron," Journal of Physics C (Proceeding of the society of London), [2], 1, 1637-1649(1968).

¹² R.L. Jacobs, "The Theory of Transition Metal Band Structures," Journal of Physics C (Proceeding of the society of London), [2], 1, 492-506(1968).

¹³ Pettifor¹⁴, and Hum and Wong are more rigorous than that achieved by Heine. However, all of these schemes originate in the work of Heine.

5. General schedule

One purpose of the present course of work is to review some original theories concerning the band structure calculations for transition metals. The justifications of the interpolation schemes from first principles have been studied. Hubbard's theory of the approximate calculation of electronic band structures for transition metals is taken as a starting point for the calculation of the total band structure energy, in which the presence of the d-bands must be explicitly considered.

Theoretically, this work is helpful to the understanding of the basis of the interpolation schemes. Further study of some other physical properties of transition metals will be facilitated by this basic understanding.

-
- ¹³ D.G. Pettifor, "An Energy-independent Method of Band-structure Calculation for Transition Metals," Journal of Physics C (Solid state physics), [2], 2, 1051-1069(1969).
- ¹⁴ D.M. Hum and K.C. Wong, "Calculation of Transition-metal Band structures," Journal of Physics C (Solid State Physics), [2], 2, 833-840(1969).

The general plan for the subsequent chapters is as follows. The Korringa-Kohn-Rostoker formulation of the band-structure calculation based on Kohn-Rostoker nonvariational method¹⁵ and also its transformation into a plane wave representation are presented in chapter II. In chapter III, Heine's physical idea for the model Hamiltonian of the interpolation scheme is described and Hubbard's scheme for the approximate calculation of electronic band structure for transition metals is formally derived. Chapter IV is devoted to an application of Hubbard's theory on the calculation of the total band structure energy for transition metals. The conclusions of the present work are summarized in this last chapter.

¹⁵ W. Kohn and N. Rostoker, "Solution of the Schrödinger Equation in periodic Lattices with an Application to Metallic Lithium," Physical Review B, 94, 1111-1120(1954).