

CHAPTER II

THE INTERPOLATION SCHEME

1. The Basis of the Interpolation Scheme

Although the interpolation scheme for the electronic energy bands of the iron-group transition metals was developed empirically^{11,12}, a firm theoretical basis has been established^{16,17,17a} through a demonstration of the connection between the equations underlying the KKR and APW methods with those characterizing the interpolation scheme.

In first-principles band calculations such as the KKR and APW methods, the crystal potential is constructed by superposing suitably chosen atomic potentials and then employing the "muffin-tin" approximation. Representing the electrons by augmented plane waves and regarding each atomic

¹⁶ V. Heine, "s-d Interaction in Transition Metals." Physical Review B, 153, 673-682 (1967).

¹⁷ J. Hubbard, "The Approximate Calculation of Electronic Band Structure." Proceedings of the Physical Society, 92, 921-937 (1967).

^{17a} Sa-nguansiri Roongkeadsakoon, "The Approximate Electronic Band Structure of Transition Metals." Unpublished Master's Thesis, Department of Physics, Chulalongkorn University, 1967.

site as an elastic scatterer characterized by a given phase shift, the band structure calculation is formulated as a scattering problem in a periodic array, as apparent in the KKR equation

$$\det \left| A_{LL'} + \kappa \delta_{LL'} \cot \delta_l \right| = 0, \quad (2.1)$$

where $A_{LL'}$, ($L = l, m$; $L' = l', m'$) are structure constants that depend solely on the symmetry of the scattering array and δ_l are phase shifts associated with each scatterer for energy $E = \kappa^2$.

Ziman¹⁸ has transformed this equation into a form appropriate to the solution of the pseudopotential formulation:

$$\det \left| \left(|\vec{k} + \vec{K}|^2 - E \right) \delta_{\vec{K}\vec{K}'} + V_{\vec{K}\vec{K}'}^P \right| = 0, \quad (2.2)$$

where

$$V_{\vec{K}\vec{K}'}^P = \sum_l \left[-\frac{(4\pi)^2}{v_a} \tan \delta_l' \right] \left[\frac{j_l(|\vec{k} + \vec{K}| r_0) j_l(|\vec{k} + \vec{K}'| r_0)}{j_l^2(\kappa r_0)} \right] \\ \times \left[\sum_m Y_L(\vec{k} + \vec{K}) Y_L^*(\vec{k} + \vec{K}') \right]$$

$$\text{and} \quad \cot \delta_l' = \cot \delta_l - \eta_l(\kappa r_0) / j_l(\kappa r_0).$$

\vec{K} and \vec{K}' are reciprocal lattice vectors, \vec{k} is the wave vector,

¹⁸ J.M. Ziman, "The T Matrix, the K Matrix, d Bands and l-dependent Pseudopotentials in the Theory of Metals." Proceedings of the Physical Society, 86, 337-353 (1965).

r_0 is the radius of the muffin-tin sphere, v_a is the volume of the unit cell, and Y_L , j_L and η_L are spherical harmonics, spherical Bessel and Neumann functions, respectively.

$V_{\vec{K}\vec{K}'}^P$ may be regarded as the plane-wave matrix elements of a pseudopotential because it depends on the scatterer through a trigonometric function of the phase shift $\delta_L(K)$ on the energy shell. A strong potential at an atomic site can be replaced by a weaker pseudopotential since the true $\delta_L(K)$ and a smaller one differing from it by integral multiples of π produce the same $V_{\vec{K}\vec{K}'}^P$.

Heine¹⁶ has expressed the plane-wave matrix elements of pseudopotential $V_{\vec{K}\vec{K}'}^P$ in the form

$$V_{\vec{K}\vec{K}'}^P = \frac{1}{E - E_d} \sum_m \gamma_{\vec{K}m}^* \gamma_{\vec{K}'m} + \sum_{\ell} \langle \vec{k} + \vec{K} | v_{P\ell} | \vec{k} + \vec{K}' \rangle + (E - E_d) \sum_m \beta_{\vec{K}m}^* \beta_{\vec{K}'m}, \quad (2.3)$$

where

$$\begin{aligned} \gamma_{\vec{K}'m} &= \langle \varphi_m | v | \vec{k} + \vec{K}' \rangle, \\ \beta_{\vec{K}'m} &= \langle \varphi_m | \vec{k} + \vec{K}' \rangle, \end{aligned}$$

E_d is a resonance energy originating from atomic d states, $|\varphi_m\rangle$ is an approximate atomic d ket, $|\vec{k} + \vec{K}\rangle$ is associated with the plane wave $\exp [i(\vec{k} + \vec{K}) \cdot \vec{r}]$, and P_{ℓ} is an operator projecting out the ℓ component.

Qualitatively, this expression may be understood in terms of the resonant scattering between the overlapping d and conduction band states. It may be seen from the schematic presentation Fig. 2-1 that, in the iron-series transition metals, the atomic d levels lie above and relatively close to the atomic zero. They act as resonant scatterers. The d character is preserved to some extent even in crystals because of the centrifugal barrier arising from the repulsive potential term $l(l+1)/r^2$ ($l=2$ for d electrons) in the Schrödinger equation. This acts as a barrier and inhibits their spread over the crystal¹⁹. This accounts for the relatively narrow width of the d band. On the other hand, for the conduction bands they are taken to be more nearly free and one expects the bottom of the conduction band, I_1 , to lie close to the muffin-tin energy. Since the d-levels in the iron-series metals lie above the muffin-tin energy, the d-bands should thus overlap the conduction bands and act as resonant scatterers for the conduction electrons.

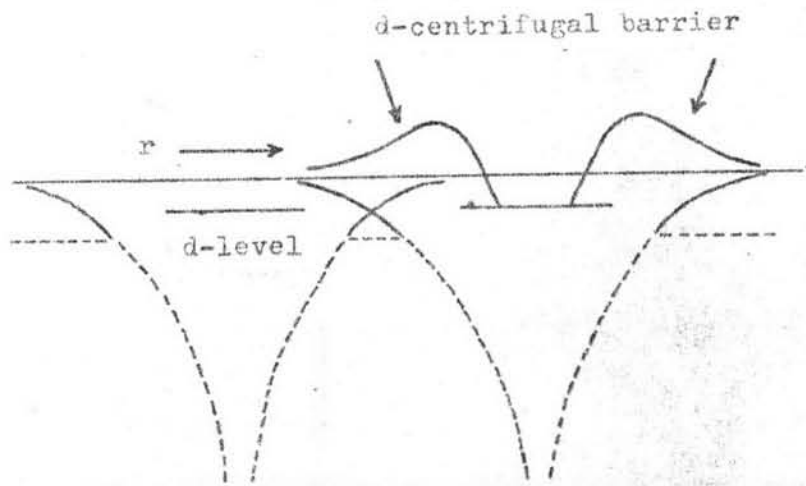
Substituting Eq.(2.2) into Eq.(2.3) we obtain the secular equation:

¹⁹ J.C. Ziman, "Some Non-Structure Aspects of the Theory of Metal." Proceedings of the Physical Society, 91, 701-723 (1967).

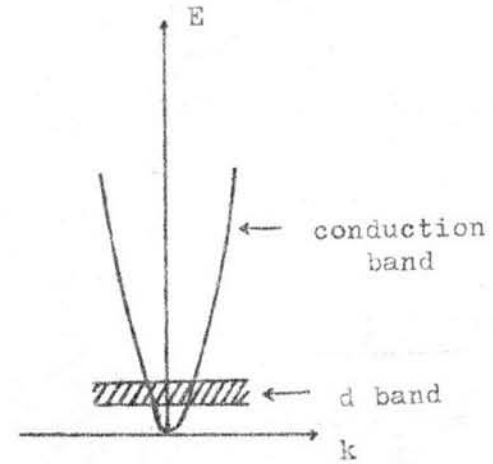
Figure 2-1

Left : The crystal potential in the muffin-tin approximation (dashed lines).

Right: The resulting conduction band and d band overlap.



Potential : Atomic —————
 Solid - - - - -



$$\det \begin{bmatrix} C_{\vec{h}\vec{h}'} & C_{\vec{h}\vec{K}'} & \gamma_{\vec{h}\vec{m}'}^* \\ \tilde{C}_{\vec{K}\vec{h}'}^* & C_{\vec{K}\vec{K}'} & \gamma_{\vec{K}\vec{m}'} \\ \tilde{\gamma}_{\vec{m}\vec{h}'} & \tilde{\gamma}_{\vec{m}\vec{K}'} & (E_d - E) \delta_{\vec{m}\vec{m}'} \end{bmatrix} = 0 \quad (2.4)$$

where

$$C_{\vec{K}\vec{K}'} = \{ |\vec{k} + \vec{K}|^2 - E \} \delta_{\vec{K}\vec{K}'} + \sum_{\vec{\ell}} \langle \vec{k} + \vec{K} | V_{P_{\vec{\ell}}} | \vec{k} + \vec{K}' \rangle + (E - E_d) \sum_m \beta_{\vec{K}\vec{m}}^* \beta_{\vec{K}'\vec{m}}$$

The rows and columns of this determinant are labelled by the magnetic quantum numbers m corresponding to $\ell = 2$ (for 3d electrons) and by the reciprocal vectors \vec{K} and \vec{h} . \vec{K} are the few smallest ones retained in the interpolation scheme in order to obtain an adequate description of the conduction bands and \vec{h} are the higher reciprocal lattice vectors which can be approximately transformed away.

The secular determinant can then be written in the form

$$\det \begin{bmatrix} C_{\vec{K}\vec{K}'} & \gamma_{\vec{K}\vec{m}'}^* \\ \tilde{\gamma}_{\vec{m}\vec{K}'} & D_{\vec{m}\vec{m}'} \end{bmatrix} = 0 \quad (2.5)$$

where

$$D_{\vec{m}\vec{m}'} \approx (E_d - E) \delta_{\vec{m}\vec{m}'} - \sum_{\vec{h}} \frac{\tilde{\gamma}_{\vec{m}\vec{h}} \gamma_{\vec{h}\vec{m}'}}{|\vec{k} + \vec{h}|^2 - E} \quad (2.6)$$

The $C_{\vec{K}\vec{K}'}$ and $\gamma_{\vec{K}\vec{m}'}$ describe the conduction bands and the

hybridization between these and the d bands, respectively.

It should be noted that the D_{mm} 's depend on the crystal potential through the hybridization γ_{hm} .

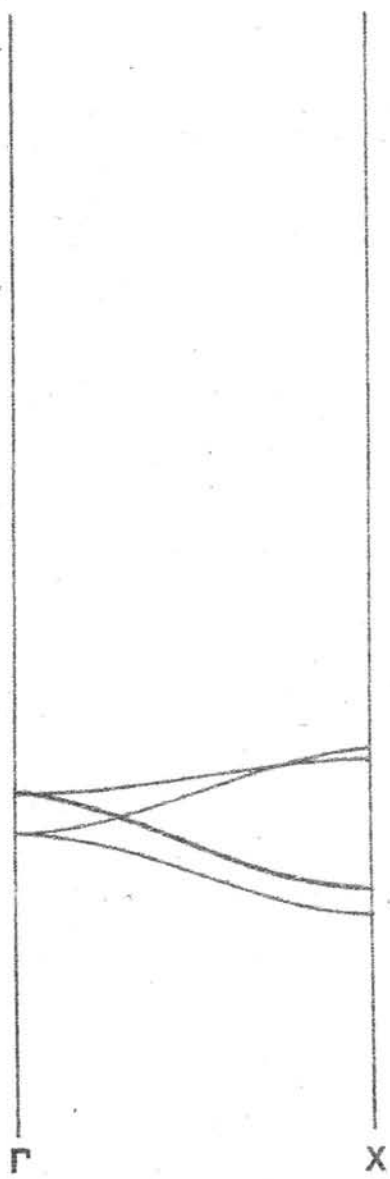
Physically the preceding transformation corresponds to the fact that the d-functions centered on each site can only interact with each other indirectly via the plane-wave states, and that the kind of overlap integrals which characterize tight-binding theory must arise from such indirect interactions. There is, therefore, a need to apportion the reciprocal lattice vectors into those \vec{K} vectors which, in addition to producing the conduction bands, provide indirect interaction among d functions centered on different sites, and the \vec{h} vectors which may be transformed away to yield the tight-binding form of the d-bands.

Hodges et al.¹¹ and Mueller¹² appeared to have arrived at an optimum separation of the reciprocal vectors, and thus made possible the retention of the minimum number of \vec{K} 's required to produce an adequate description of the conduction bands while permitting the description of the d-bands in the nearest-neighbor approximation.

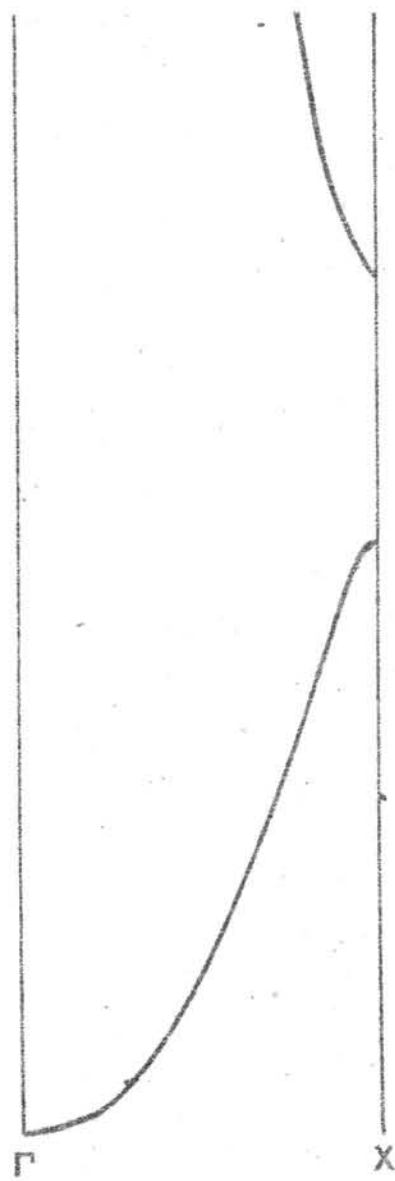
The physical content of the above formalism may be shown pictorially in Fig.2-2, which depicts the band structures of a paramagnetic fcc metal in the [100] direction. The d and conduction bands are shown respectively in Figs.2-2a and 2-2b. These can be obtained from a solution of the D_{mm} 's and $C_{\vec{K}\vec{K}'}$ blocks of Eq.(2.5). Figure 2-2c shows the actual bands after

Figure 2-2

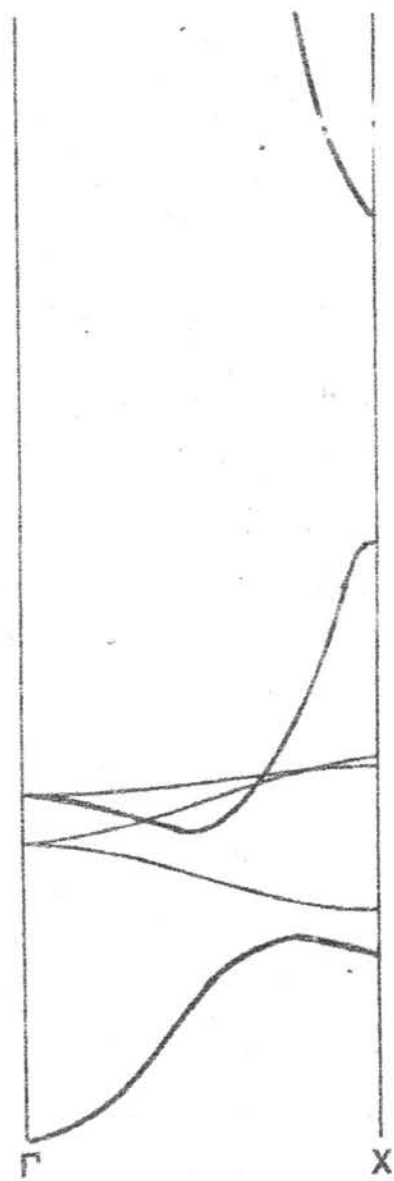
Fcc transition metal d bands, conduction bands, and hybridized bands in (a), (b), and (c), respectively.



(a)



(b)



(c)

hybridization. The heavy lines are the bands having the same symmetry.

Eq.(2.5) is closely related to the secular equation of the interpolation scheme, Eq.(2.24). For fcc lattice, this determinant is 9×9 and contains four plane waves labelled by \vec{k} and five d functions labelled by m .

2 The Framework

The interpolation scheme for the band structures of transition metals to be employed in the present work will be set up for an fcc lattice for $1/48$ of the Brillouin zone in which $k_y \geq k_x \geq k_z \geq 0$ as shown in Fig.2-3. All other points of the reciprocal lattice are related to points in this part of the zone by symmetry transformations.

Because of the limitation to the paramagnetic state, all electron correlation effects, spin-orbit interactions and other relativistic effects are neglected. Instead of using the full many-electron Hamiltonian, we consider only the one-electron Hartree-Fock Hamiltonian, denoted by

$$H = H_{\text{band}} \quad , \quad (2.7)$$

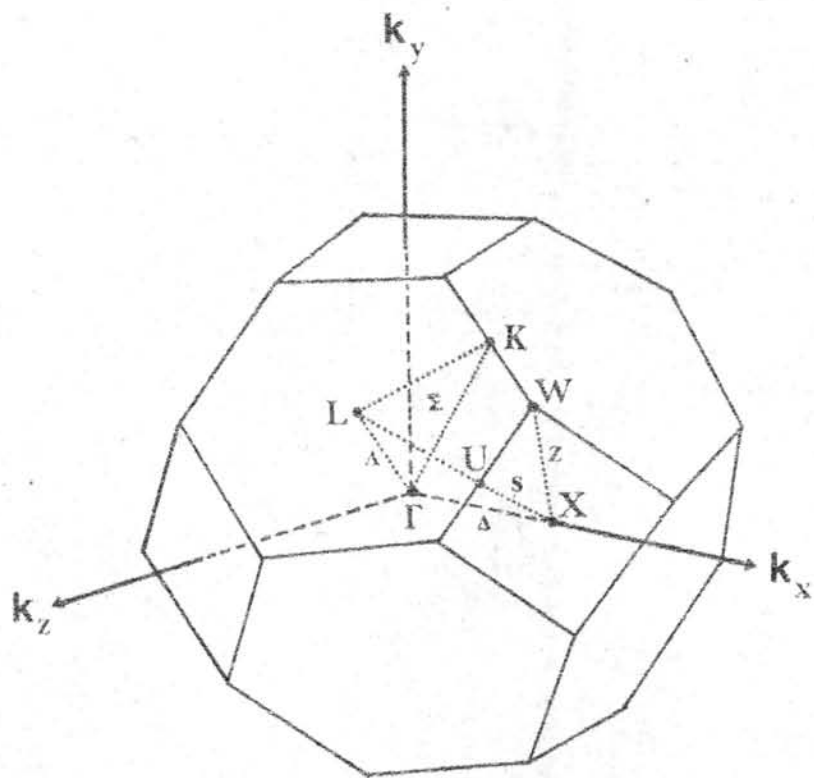
which gives the results of ordinary nonrelativistic band theory. The eigenvalue equation corresponding to H_{band} is represented by

$$H B_{\vec{k}m}(\vec{r}) = E_m(\vec{k}) B_{\vec{k}m}(\vec{r}) \quad (2.8)$$

where m is the band index, $E_m(\vec{k})$ is the eigenvalue or the band energy of the m th band, and the Bloch eigenfunctions $B_{\vec{k}m}(\vec{r})$, according to the theoretical considerations of the previous section, are linear combinations of the LCAO's $b_{\vec{k}n}(\vec{r})$ and the OPW's $b_{\vec{k}K}(\vec{r})$:

Figure 2-3

The $1/48$ primitive cell in the Brillouin zone of the fcc lattice in which $k_y \geq k_x \geq k_z \geq 0$.



$$B_{\vec{k}m}(\vec{r}) = \sum_n a_{mn}(\vec{k}) b_{\vec{k}n}(\vec{r}) + \sum_K a_{mK}(\vec{k}) b_{\vec{k}K}(\vec{r}) . \quad (2.9)$$

The LCAO's are

$$b_{\vec{k}n}(\vec{r}) = \langle \vec{r} | \vec{k}n \rangle = N^{-\frac{1}{2}} \sum_{\ell} e^{i\vec{k} \cdot \vec{R}_{\ell}} \varphi_n(\vec{r} - \vec{R}_{\ell}) \quad (2.10)$$

where \vec{R}_{ℓ} labels the positions of the atoms in the solid, $n = 1, \dots, 5$, labels the atomic 3d orbitals, $\varphi_n(\vec{r} - \vec{R}_{\ell})$, centered at site \vec{R}_{ℓ} and the summation is over all atoms, totaling N .

The usual convention of solid state physics is used and φ_n are chosen as the basis functions for the irreducible representations of the cubic point group. Specifically, the d basis functions will be written in the form

$$\varphi_n(\vec{r}) = C_n F_n(x/r, y/r, z/r) g(r) , \quad (2.11)$$

with the normalization factors C_n and the cubic harmonics F_n chosen as follows:

n	C_n	F_n	
1	1	$\frac{x}{r} \cdot \frac{y}{r}$	
2	1	$\frac{y}{r} \cdot \frac{z}{r}$	
3	1	$\frac{z}{r} \cdot \frac{x}{r}$	(2.11.A)
4	$\frac{1}{2}$	$[(x/r)^2 - (y/r)^2]$	
5	$\frac{1}{2}\sqrt{3}$	$[3(z/r)^2 - 1]$	

and $g(r)$ contains the radial function for 3d electrons and the remaining constants. The present notation is thus slightly different from the more common notations:

$$\begin{aligned}
 \varphi_1(\vec{r}) &= (15/4\pi)^{\frac{1}{2}} \frac{x}{r} \cdot \frac{y}{r} f(r) \quad , \\
 \varphi_2(\vec{r}) &= (15/4\pi)^{\frac{1}{2}} \frac{y}{r} \cdot \frac{z}{r} f(r) \quad , \\
 \varphi_3(\vec{r}) &= (15/4\pi)^{\frac{1}{2}} \frac{z}{r} \cdot \frac{x}{r} f(r) \quad , \quad (2.11.5) \\
 \varphi_4(\vec{r}) &= (15/16\pi)^{\frac{1}{2}} \left(\frac{x^2}{r^2} - \frac{y^2}{r^2} \right) f(r) \quad , \\
 \varphi_5(\vec{r}) &= (5/16\pi)^{\frac{1}{2}} \left(\frac{3z^2}{r^2} - 1 \right) f(r) \quad ,
 \end{aligned}$$

which satisfy

$$\left[\frac{p^2}{2m} + U(\vec{r}) \right] \varphi_n(\vec{r}) = E_{\text{atomic}} \varphi_n(\vec{r}) \quad (2.12)$$

where $U(\vec{r})$ is the atomic potential and the $f(r)$ is the normalized radial function of the isolated atom:

$$\int_0^{\infty} [rf(r)]^2 dr = 1 \quad . \quad (2.13)$$

It is to be noted that with our choice of breaking up the normalization constants, we have

$$\begin{aligned}
 \sum_{n=1}^5 \left| C_n \varphi_n(\vec{r}) \right|^2 &= \frac{1}{r^4} \left[x^2 y^2 + y^2 z^2 + z^2 x^2 + \frac{1}{4} (x^2 - y^2)^2 \right. \\
 &\quad \left. + \frac{1}{12} (3z^2 - r^2)^2 \right] = \frac{1}{3} \quad . \quad (2.14)
 \end{aligned}$$

The OPW's have the form

$$b_{\vec{k}\vec{K}}(\vec{r}) = c_{\vec{k}\vec{K}}^{-1} [\langle \vec{r} | \vec{k} + \vec{K} \rangle - \sum_{\mu} \langle \vec{r} | \vec{k}\mu \rangle \langle \vec{k}\mu | \vec{k} + \vec{K} \rangle] \quad (2.15)$$

where the \vec{K} are the reciprocal lattice vectors and the normalization factor is

$$|c_{\vec{k}\vec{K}}|^{-2} = 1 - \sum_{\mu} |\langle \vec{k}\mu | \vec{k} + \vec{K} \rangle|^2 \quad (2.16)$$

The first terms in the OPW's :

$$\langle \vec{r} | \vec{k} + \vec{K} \rangle = \frac{1}{(N v_a)^{\frac{1}{2}}} e^{i(\vec{k} + \vec{K}) \cdot \vec{r}} \quad (2.17)$$

are the plane waves where v_a is the volume of the unit cell.

The index μ runs over all core states including the 3d states: 1s, 2s,, 3d. This is so that the OPW's are really orthogonal to all core and 3d states.

In principle, if the basis is to be fully orthogonal, all the OPW's should also be orthogonalized to each other. In practice, a satisfactory interpolation scheme may be obtained without explicitly carrying out these various orthogonalization steps. In the 1/48 of the Brillouin zone being used for developing the interpolation scheme, it is sufficient to use only four OPW's: those with the following \vec{K} values:

$$\begin{aligned}
 \vec{k}_1 &= \frac{\pi}{4a} (0,0,0) & , \\
 \vec{k}_2 &= \frac{\pi}{4a} (0,-16,0) & , \\
 \vec{k}_3 &= \frac{\pi}{4a} (-8,-8,-8) & , \\
 \vec{k}_4 &= \frac{\pi}{4a} (-8,-8,8) & .
 \end{aligned}
 \tag{2.18}$$

These are the reciprocal lattice vectors \vec{k} forming the symmetrized linear combinations of orthogonalized plane waves that give the lowest energy empty-lattice eigenfunctions. This "4-OPW approximation" was first used by Harrison to calculate the energy bands for Al²⁰. The explicit forms of the OPW's may be found in Appendix A.

Mueller¹² has introduced an important simplifying ansatz; namely, the radial d-wave functions in a given atomic cell are the same for all $|\vec{k}|$ and are independent of the band index m . Thus the d states are regarded as part of the spherically symmetric atomic core. This ansatz was justified by the accuracy of the interpolation scheme so developed.

Since the other core states are much lower in energy than the 3d states, Mueller wrote the OPW's, in a slightly different notation, in the form [see (2.15)]

²⁰ W.A. Harrison, "Band Structure of Aluminum." Physical Review B, 118, 1182-1189 (1960).

$$|\Phi_{\vec{k}}\rangle = c_{\vec{k}}^{-1} [|\vec{k}\rangle - \sum_n M_n(\vec{k}) |n\rangle] \quad (2.19)$$

where $M_n(\vec{k})$ are the orthogonality coefficients:

$$M_n(\vec{k}) = \langle \psi_n | \vec{k} \rangle \quad (2.20)$$

Using the completeness relation, we write (2.20) in the form

$$M_n(\vec{k}) = \int \langle \psi_n | \vec{r} \rangle \langle \vec{r} | \vec{k} \rangle d\vec{r} ,$$

where $\langle \vec{r} | \psi_n \rangle$ and $\langle \vec{r} | \vec{k} \rangle$ denote respectively a d function and a plane wave. To evaluate this integral, it is convenient to expand the plane wave in terms of spherical harmonics and spherical Bessel functions:

$$\begin{aligned} \langle \vec{r} | \vec{k} \rangle &= e^{i\vec{k} \cdot \vec{r}} = 4\pi \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} j_l(kr) \\ &\quad \times Y_{lm}^*(\theta_k, \phi_k) Y_{lm}(\theta_r, \phi_r) . \end{aligned}$$

Then, using the completeness relation

$$\int |\vec{r}\rangle \langle \vec{r}| d\vec{r} = 1 ,$$

the orthogonality condition of the spherical harmonics

$$\int Y_{l'm'}^*(\Omega) Y_{lm}(\Omega) d\Omega = \delta_{ll'} \delta_{mm'} ,$$

and the form of the d functions in (2.11), we obtain the orthogonality coefficient in the form

$$M_n(\vec{k}) = C_n F_n(k_x/k, k_y/k, k_z/k) f(k) \quad (2.21)$$

where

$$f(k) = \int_0^\infty j_2(kr) g(r) r^2 dr \quad (2.22)$$

It is to be noted that because of the d-isotropy ansatz, f is function of the magnitude k and not of the vector \vec{k} .

To summarize, the Bloch eigenfunctions $B_{\vec{k}m}(\vec{r})$ to be used for evaluating the band structures are to be spanned by the 9 basis functions, consisting of the 5 d-orbitals:

$$\varphi_n(\vec{r}) = C_n F_n(x/r, y/r, z/r) g(r), \quad n = 1, \dots, 5,$$

and the 4 OPW's

$$\begin{aligned} b_{\vec{k}\vec{K}_1}(\vec{r}) &= C_{\vec{k}\vec{K}_1}^{-1} [\langle \vec{r} | \vec{k} + \vec{K}_1 \rangle - \sum_n M_n(\vec{k} + \vec{K}_1) \langle \vec{r} | \vec{n} \rangle], \quad i = 1, \dots, 4 \\ &= C_{\vec{k}\vec{K}_1} \left[\frac{1}{\sqrt{\Omega}} e^{i(\vec{k} + \vec{K}_1) \cdot \vec{r}} - \sum_n M_n(\vec{k} + \vec{K}_1) \varphi_n(\vec{r}) \right] \end{aligned}$$

where the vectors \vec{K}_1 are listed in Eq.(2.18) and $\Omega = Nv_a$.

For convenience, we introduce the new running index ν to indicate the various basis functions used in our work:

$$\langle \vec{r} | \vec{k}\nu \rangle = b_{\vec{k}\nu}(\vec{r}) .$$

For $\nu = 1, 2, 3, 4$, $b_{\vec{k}\nu}(\vec{r})$ are the 4 OPW's corresponding to $\vec{K}_1, \vec{K}_2, \vec{K}_3$, and \vec{K}_4 as listed in Eq.(2.18) respectively.

For $\nu = 5, 6, 7, 8, 9$, $b_{\vec{k}\nu}(\vec{r})$ are the 5 LCAO's corresponding to $\varphi_1, \varphi_2, \varphi_3, \varphi_4$, and φ_5 as listed in Eqs.(2.11) and (2.11.A) respectively.

The energy eigenvalues are given by the solutions of the secular equation

$$\det \left| \langle \vec{k}\nu | H-E | \vec{k}\nu' \rangle \right| = \det \left| \langle \vec{k}\nu | H | \vec{k}\nu' \rangle - E(\vec{k}) \langle \vec{k}\nu | \vec{k}\nu' \rangle \right| = 0 . \quad (2.23)$$

We will assume throughout that the 9 basis functions form an orthonormal set, then the secular equation becomes

$$\det \left| \langle \vec{k}\nu | H | \vec{k}\nu' \rangle - E(\vec{k}) \delta_{\nu\nu'} \right| = 0 . \quad (2.24)$$

This is a 9x9 matrix equation. This is the point of departure for the interpolation scheme which was utilized by Hodges and by Mueller and which was justified by Heine and Hubbard in the form of (2.5).

The entire matrix may be written schematically in the form :

$$\left| \langle \vec{k}\nu | H | \vec{k}\nu' \rangle \right| = \left(\begin{array}{c|c} \text{OPW - OPW} & \text{OPW - LCAO} \\ \hline \text{[OPW - LCAO]}^\dagger & \text{LCAO - LCAO} \end{array} \right)$$

H ₁₁	H ₁₂	H ₁₃	H ₁₄	H ₁₅	H ₁₆	H ₁₇	H ₁₈	H ₁₉
H ₂₁	H ₂₂	H ₂₃	-	H ₂₅	H ₂₆	H ₂₇	H ₂₈	-
H ₃₁	H ₃₂	-	-	H ₃₅	H ₃₆	-	-	-
H ₄₁	-	-	-	H ₄₅	-	-	-	-
H ₅₁	H ₅₂	H ₅₃	H ₅₄	H ₅₅	H ₅₆	H ₅₇	H ₅₈	H ₅₉
-	-	-	-	-	-	-	-	-
-	-	-	-	-	-	-	-	-
-	-	-	-	-	-	-	-	-
H ₉₁	-	-	H ₉₄	H ₉₅	-	-	-	H ₉₉

(2.25)



3 The LCAO-LCAO Block

To obtain the matrix elements in the LCAO-LCAO block, the tight-binding approximation as used by Fletcher²¹ and by Slater and Koster²² will be employed. The crystal potential may be written as a superposition of atomic potentials centered about sites \vec{R}_ℓ ,

$$V(\vec{r}) = \sum_{\ell} U(\vec{r} - \vec{R}_\ell) \quad . \quad (2.26)$$

The matrix elements can be obtained by using the LCAO's as shown in Eq.(2.10), for $n, n' = 1, 2, 3, 4, 5$, as follows:

$$\begin{aligned} H_{nn'}(\vec{k}) &= \left\langle \vec{k}n \left| \frac{p^2}{2m} + V(\vec{r}) \right| \vec{k}n' \right\rangle \\ &= \int N^{-\frac{1}{2}} \sum_{\ell} e^{-i\vec{k} \cdot \vec{R}_\ell} \varphi_n^*(\vec{r} - \vec{R}_\ell) \\ &\quad \times \left[\frac{p^2}{2m} + V(\vec{r}) \right] N^{-\frac{1}{2}} \sum_{\ell'} e^{i\vec{k} \cdot \vec{R}_{\ell'}} \varphi_{n'}(\vec{r} - \vec{R}_{\ell'}) d\vec{r} \end{aligned}$$

²¹ G.C. Fletcher, "Density of States Curve for the 3d Electrons in Nickel." Proceedings of the Physical Society of London, A65, 192-202 (1952); G.C. Fletcher and E.P. Wohlfarth, Philosophical Magazine, 42, 106 (1951).

²² J.C. Slater and G.F. Koster, "Simplified LCAO Method for the Periodic Potential Problem." Physical Review B, 94, 1498-1524 (1954).

$$\begin{aligned}
&= \int \varphi_n^*(\vec{r}) \left[\frac{p^2}{2m} + v(\vec{r}) \right] \varphi_n(\vec{r}) d\vec{r} \\
&\quad + \sum_{\ell \neq 0} e^{-i\vec{k} \cdot \vec{R}_\ell} \int \varphi_n^*(\vec{r} - \vec{R}_\ell) \left[\frac{p^2}{2m} + v(\vec{r}) \right] \varphi_n(\vec{r}) d\vec{r} \\
&= [E_0 + \Delta (\delta_{n4} + \delta_{n5})] \delta_{nn} \\
&\quad + \sum_{\ell \neq 0} e^{-i\vec{k} \cdot \vec{R}_\ell} \int \varphi_n^*(\vec{r} - \vec{R}_\ell) (v - U) \varphi_n(\vec{r}) d\vec{r} .
\end{aligned} \tag{2.27}$$

We have used

$$\begin{aligned}
&\int \varphi_n^*(\vec{r}) \left[\frac{p^2}{2m} + v(\vec{r}) \right] \varphi_n(\vec{r}) d\vec{r} \\
&= \begin{cases} E_0 & , \text{ for } n = 1, 2, 3 \text{ (} t_{2g} \text{ orbital) ,} \\ E_0 + \Delta & , \text{ for } n = 4, 5 \text{ (} e_g \text{ orbital) ,} \end{cases}
\end{aligned}$$

where Δ is the crystal field splitting of the d bands at the point Γ in the cubic environment.

If only nearest-neighbor interactions are retained, the overlap integrals involved in a fcc structure are :

$$\begin{aligned}
A_1 &= -\int \varphi_1^*(x - \frac{a}{2}, y - \frac{a}{2}, z)(V - U) \varphi_1(x, y, z) d\vec{r} , \\
A_2 &= \int \varphi_1^*(x, y - \frac{a}{2}, z - \frac{a}{2})(V - U) \varphi_1(x, y, z) d\vec{r} , \\
A_3 &= \int \varphi_1^*(x - \frac{a}{2}, y, z - \frac{a}{2})(V - U) \varphi_2(x, y, z) d\vec{r} , \\
A_4 &= \int \varphi_4^*(x - \frac{a}{2}, y - \frac{a}{2}, z)(V - U) \varphi_4(x, y, z) d\vec{r} , \\
A_5 &= -\int \varphi_4^*(x, y - \frac{a}{2}, z - \frac{a}{2})(V - U) \varphi_4(x, y, z) d\vec{r} , \\
A_6 &= \int \varphi_2^*(x, y - \frac{a}{2}, z - \frac{a}{2})(V - U) \varphi_4(x, y, z) d\vec{r} .
\end{aligned}$$

The explicit matrix elements of the LCAO-LCAO block then have the forms (note that $\nu = n + 4$) :

$$\begin{aligned}
 H_{\nu\nu'} : \quad H_{55} &= E_0 - 4A_1 \cos \eta \cos \xi + 4A_2 \cos \varphi (\cos \xi + \cos \eta) \\
 H_{66} &= E_0 - 4A_1 \cos \eta \cos \varphi + 4A_2 \cos \xi (\cos \eta + \cos \varphi) \\
 H_{77} &= E_0 - 4A_1 \cos \xi \cos \varphi + 4A_2 \cos \eta (\cos \xi + \cos \varphi) \\
 H_{88} &= E_0 + \Delta + 4A_4 \cos \xi \cos \eta - 4A_5 \cos \varphi (\cos \xi + \cos \eta) \\
 H_{99} &= E_0 + \Delta - (4/3)(A_4 + 4A_5) \cos \xi \cos \eta \\
 &\quad + (4/3)(2A_4 - A_5) \cos \varphi (\cos \xi + \cos \eta) \\
 H_{56} &= H_{65} = -4A_3 \sin \xi \sin \varphi \\
 H_{57} &= H_{75} = -4A_3 \sin \eta \sin \varphi \\
 H_{58} &= H_{85} = 0 \qquad (2.29) \\
 H_{59} &= H_{95} = -(8/\sqrt{3})A_6 \sin \xi \sin \eta \\
 H_{67} &= H_{76} = -4A_3 \sin \xi \sin \eta \\
 H_{68} &= H_{86} = -4A_6 \sin \eta \sin \varphi \\
 H_{69} &= H_{96} = (4/\sqrt{3})A_6 \sin \eta \sin \varphi \\
 H_{78} &= H_{87} = 4A_6 \sin \xi \sin \varphi \\
 H_{79} &= H_{97} = (4/\sqrt{3})A_6 \sin \xi \sin \varphi \\
 H_{89} &= H_{98} = (4/\sqrt{3})(A_4 + A_5) \cos \varphi (\cos \eta - \cos \xi) ,
 \end{aligned}$$

where the coordinates are

$$\xi = (a/2)k_x, \quad \eta = (a/2)k_y, \quad \zeta = (a/2)k_z. \quad (2.30)$$

The interpolation scheme refers to the fact that the values of the overlap integrals A_1, A_2, \dots, A_6 , as well as the position of the d-level (E_0), and the crystal field splitting (Δ), are regarded as adjustable parameters.

In the LCAO-LCAO block of the secular determinant, $A_1, \dots, A_6, E_0, \Delta$ are the 8 interpolation parameters introduced.

4 The OPW-OPW Block

The matrix elements in the OPW-OPW block are to be expressed in paramagnetic forms as follows. Using (2.19) and writing $\vec{k}_{\nu} = \vec{k} + \vec{k}_{\nu}$, we have, for $\nu, \nu' = 1, \dots, 4$,

$$\begin{aligned}
 H_{\nu\nu'} &= \langle \vec{k}_{\nu} | H | \vec{k}_{\nu'} \rangle \\
 &= C_{\vec{k}_{\nu}}^{-1} C_{\vec{k}_{\nu'}}^{-1} [\langle \vec{k}_{\nu} | -\sum_n M_n^*(\vec{k}_{\nu}) \langle n |] \\
 &\quad \times H [|k_{\nu'}\rangle - \sum_n M_n(\vec{k}_{\nu'}) | n'\rangle] \\
 &= C_{\vec{k}_{\nu}}^{-1} C_{\vec{k}_{\nu'}}^{-1} [\langle \vec{k}_{\nu} | H | \vec{k}_{\nu'} \rangle - \sum_n M_n^*(\vec{k}_{\nu}) \langle n | H | \vec{k}_{\nu'} \rangle \\
 &\quad - \sum_{n'} M_n(\vec{k}_{\nu'}) \langle \vec{k}_{\nu} | H | n' \rangle \\
 &\quad + \sum_{n, n'} M_n^*(\vec{k}_{\nu}) M_n(\vec{k}_{\nu'}) \langle n | H | n' \rangle \quad . \quad (2.31)
 \end{aligned}$$

We shall denote this in the form

$$\langle \vec{k}_{\nu} | H | \vec{k}_{\nu'} \rangle = C_{\vec{k}_{\nu}}^{-1} C_{\vec{k}_{\nu'}}^{-1} [H^I + H^{II} + H^{III} + H^{IV}] \quad (2.32)$$

with

$$\begin{aligned}
 H^I &= \langle \vec{k}_{\nu} | H | \vec{k}_{\nu'} \rangle \\
 H^{II} + H^{III} &= - \sum_n M_n^*(\vec{k}_{\nu}) \langle n | H | \vec{k}_{\nu'} \rangle - \sum_{n'} M_n(\vec{k}_{\nu'}) \langle \vec{k}_{\nu} | H | n' \rangle \\
 H^{IV} &= \sum_{n, n'} M_n^*(\vec{k}_{\nu}) M_n(\vec{k}_{\nu'}) \langle n | H | n' \rangle \quad .
 \end{aligned} \quad (2.33)$$

We express the crystal potential in the form of Fourier expansion of the pseudopotential :

$$V(\vec{r}) = V_p(\vec{r}) = \sum_{\vec{K}'} V_{\vec{K}'} e^{i\vec{K}' \cdot \vec{r}} \quad (2.34)$$

For $\nu = \nu'$, $H^I = \langle \vec{k}_\nu | H | \vec{k}_\nu \rangle$ can be expressed in the form

$$\begin{aligned} H^I &= \frac{1}{Nv_a} \int e^{-i(\vec{k} + \vec{K}_\nu) \cdot \vec{r}} \left[\frac{p^2}{2m} + \sum_{\vec{K}'} V_{\vec{K}'} e^{i\vec{K}' \cdot \vec{r}} \right] \\ &\quad \times e^{i(\vec{k} + \vec{K}_\nu) \cdot \vec{r}} d\vec{r} \\ &= \frac{\hbar^2}{2m} \left(\frac{\pi}{4a} \right)^2 |\vec{k} + \vec{K}_\nu|^2 + \sum_{\vec{K}'} \left\{ \frac{1}{Nv_a} \int V_{\vec{K}'} e^{i\vec{K}' \cdot \vec{r}} d\vec{r} \right\} \\ &= \frac{\hbar^2}{2m} \left(\frac{\pi}{4a} \right)^2 |\vec{k} + \vec{K}_\nu|^2 + \sum_{\vec{K}'} V_{\vec{K}'} \delta(\vec{K}') \\ &= \frac{\hbar^2}{2m} \left(\frac{\pi}{4a} \right)^2 |\vec{k} + \vec{K}_\nu|^2 + V_0 \end{aligned}$$

Two parameters are introduced at this point, namely

$$\begin{aligned} \alpha &= \frac{\hbar^2}{2m} \left(\frac{\pi}{4a} \right)^2 \\ \beta &= V_0 = \frac{1}{Nv_a} \int V(\vec{r}) d\vec{r} \end{aligned} \quad (2.35)$$

so that the diagonal terms of $H^I = \langle \vec{k}_\nu | H | \vec{k}_\nu \rangle$ are directly parametrized in the form of a simple free-electron-like parabola

$$\begin{aligned}
 H^I &= \langle \vec{k}_\nu | H | \vec{k}_\nu \rangle \\
 &= \alpha |\vec{k} + \vec{K}|^2 + \beta
 \end{aligned}$$

where α determines the width of the parabola and β determines the location of the bottom of the parabola. The parameters α and β are discussed further later on.

For $\nu \neq \nu'$, H^I can be expressed as follows :

$$\begin{aligned}
 H^I &= \frac{1}{Nv_a} \int e^{-i(\vec{k} + \vec{K}_\nu) \cdot \vec{r}} \left[\frac{p^2}{2m} + \sum_{\vec{K}'} \frac{V_{\vec{K}'}}{K'} e^{i\vec{K}' \cdot \vec{r}} \right] \\
 &\quad \times e^{i(\vec{k} + \vec{K}_\nu) \cdot \vec{r}} d\vec{r} \\
 &= \frac{1}{Nv_a} \sum_{\vec{K}'} \frac{V_{\vec{K}'}}{K'} \int e^{i[\vec{K}' - (\vec{K}_\nu - \vec{K}_\nu')] \cdot \vec{r}} d\vec{r} \\
 &= \sum_{\vec{K}'} \frac{V_{\vec{K}'}}{K'} \delta_{[\vec{K}' - (\vec{K}_\nu - \vec{K}_\nu')] } \\
 &= \frac{V_{\vec{K}_\nu - \vec{K}_\nu'}}{K_{\vec{K}_\nu - \vec{K}_\nu'}} \quad (2.36)
 \end{aligned}$$

\vec{K}_ν refers to one of the reciprocal vectors, expressed in units of $\left(\frac{\pi}{4a}\right)$, as listed in Eq.(2.18). The terms $\frac{V_{\vec{K}'}}{K'}$ represent the sums of the matrix elements of the crystal potential and the repulsive potential between two plane waves characterized by wave vectors differing in wave-numbers by $\vec{K}_\nu - \vec{K}_\nu'$. They are formed by replacing the real crystal potential with the weaker pseudopotential. For the 4 OPW's that are involved, the wave-vector differences are such that only two Fourier coefficients, namely V_{111} and V_{200} , need be employed. In the spirit of

Harrison's work²⁰, the matrix elements V_{111} and V_{200} are regarded as adjustable parameters.

The diagonal matrix elements $H_{\nu\nu}'(\vec{k}) = \beta + \alpha |\vec{k} + \vec{K}|^2$ are viewed as giving rise to a simple parabolic band such as that of the free-electron gas, in which case $V(\vec{r}) = 0$ and $\alpha = \frac{\hbar^2}{2m} \left(\frac{\pi}{4a}\right)^2$. However, if the terms H^{II} , H^{III} and H^{IV} are included explicitly, the diagonal matrix elements are not simply equal to the pseudopotential parameters V_{111} and V_{200} . All the matrix elements in the OPW-OPW block now include complicated terms involving normalization factors $C_{\vec{k}}$ such as those given in Eq.(2.16), orthogonality integrals $M_n(\vec{k})$ such as those given in Eq.(2.21), and hybridization integrals between OPW's and LCAO's.

In Hodges' work, the orthogonalization effects were included in a simplified manner. Instead of the OPW's, plane waves were used. The effects of orthogonalization were included in an approximate way through adjusting the values of α , V_{111} and V_{200} . The parameter β is just a constant fixing the zero of energy. All this amounts to a direct parametrization of the $E(\vec{k})$ function.

In the present work, explicit orthogonalization of the conduction band states to the d-band states is carried out explicitly, following Mueller. However, α is taken as a fixed constant whose value depends on lattice constant as in Eq.(2.35). This is the reason our value of α differs slightly from that appearing in the Hodges scheme¹¹ in which α was an adjustable parameter.

Next, we consider

$$H^{IV} = \sum_{n, n'} M_n^*(\vec{k}_\nu) M_{n'}(\vec{k}_\nu) \langle n | H | n' \rangle .$$

Using (2.21), we have

$$H^{IV} = \left[\sum_{n, n'} C_n C_{n'} F_n(\vec{k}_\nu) F_{n'}(\vec{k}_\nu) H_{nn'} \right] f(k_\nu) f(k_\nu), \quad (2.37)$$

where $H_{nn'} = \langle n | H | n' \rangle$.

Following Mueller's work, we introduce the isotropic hybridization form factor $g(k)$ through

$$\langle n | H | \vec{k}_\nu \rangle = C_n F_n(\vec{k}_\nu) g(k_\nu) \quad , \quad \nu = 1, \dots, 4. \quad (2.38)$$

This is again based on the ansatz of d-isotropy and amounts to the neglect of nearest-neighbor overlap in the hybridization term. The mixing is regarded as having been derived from interactions in a spherically symmetric central cell.

We have, using Eq.(2.19),

$$\langle n | H | \vec{k}_\nu \rangle = C_n^{-1} \left[\langle n | H | \vec{k}_\nu \rangle - \sum_{n'} H_{nn'} M_{n'}(\vec{k}_\nu) \right]$$

giving

$$\langle n | H | \vec{k}_\nu \rangle = C_n \langle n | H | \vec{k}_\nu \rangle + \sum_{n'} H_{nn'} M_{n'}(\vec{k}_\nu) .$$

Thus

$$H^{II} + H^{III} = H^V - 2H^{IV} \quad (2.40)$$

where

$$H^V = - \sum_n C_n C_n F_n(k_{\nu}) F_n(k_{\nu}') [C_{\vec{k}_{\nu}'} g(k_{\nu}') f(k_{\nu}) + C_{\vec{k}_{\nu}} g(k_{\nu}) f(k_{\nu}')] \quad .$$

From Eqs.(2.11) and (2.21), we can see that because of d-isotropy, as $k \rightarrow 0$, $f(k)$ is of order k^2 . Mueller has found that it would be convenient to represent $f(k)$ by

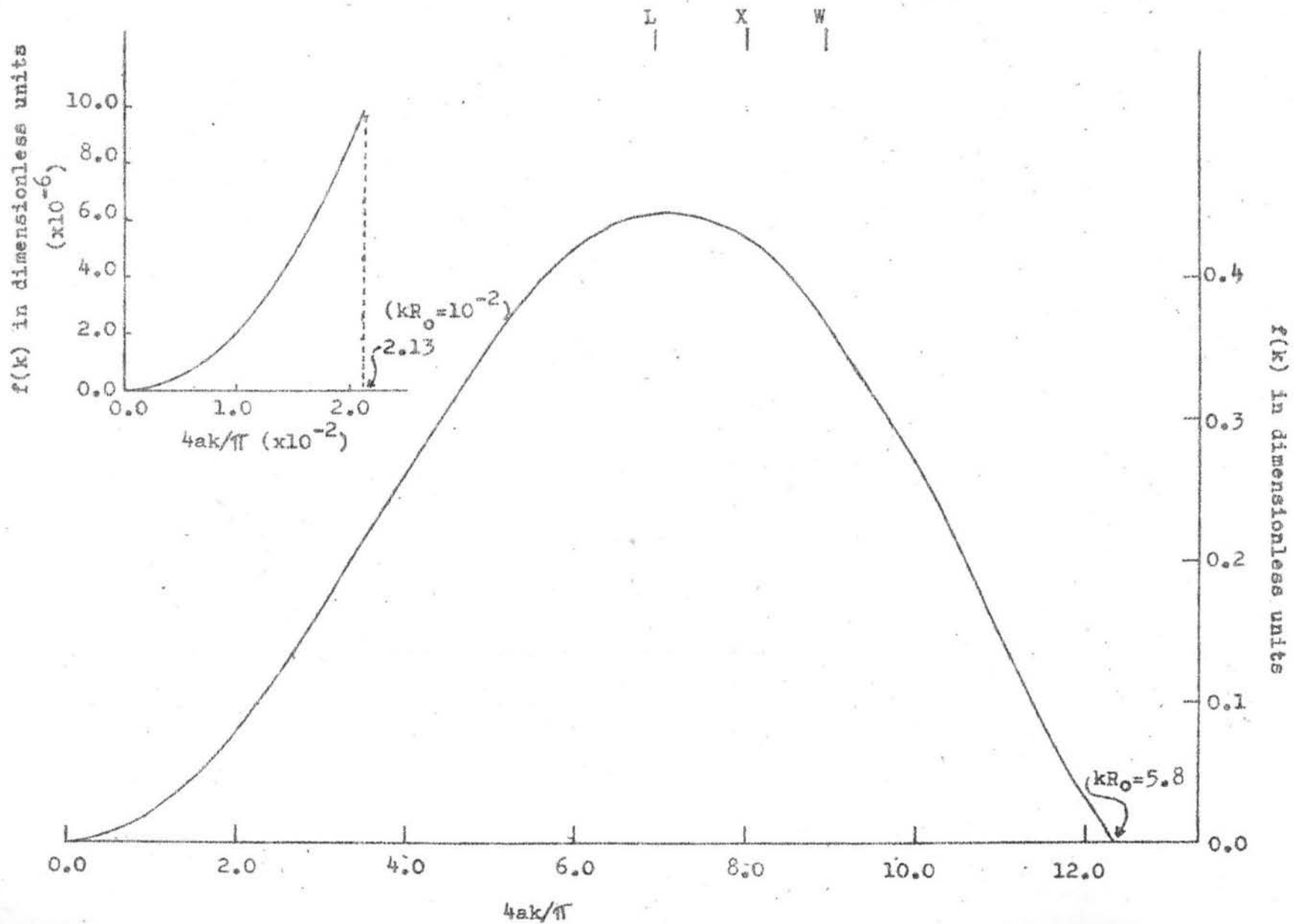
$$f(k) = K_0 j_2(kR_0) \quad (2.41)$$

where R_0 and K_0 are adjustable parameters, and $j_2(x)$ is the second spherical Bessel function obtained by expanding the plane waves in terms of Legendre polynomials. Mueller found that the energy bands in the range of interest are not greatly affected by interactions for $k \geq 2L$ (twice the length of the L direction in 1/48 of the Brillouin zone). The convergence of the overlap form factor may be improved in the range under consideration if $f(k)$ is cut off beyond its second node. The explicit form of $f(k)$ used by Mueller to fit Burdick's calculation of Cu is shown schematically in Fig.2-4 .

Similarly for $g(k)$, introduced in (2.38), it can also be shown that, as $k \rightarrow 0$, $g(k) \rightarrow k^2$ and thus for small k , the explicit form of $g(k)$ can be written

Figure 2-4

The orthogonalization form factor $f(k)$. Note that it peaks near the zone edges. The small insert shows the value at region of small k . The cut-off point is also shown in the figure. The value of $f(k)$ shown is for a fit of Burdick's Cu bands. The explicit algebraic form can be seen in Subroutine RF listed in Appendix C.



$$g(k) = K_1 j_2(kR_1) \quad (2.42)$$

where K_1 and R_1 are again adjustable parameters. The hybridization form factor $g(k)$ for Cu, used by Mueller to fit Burdick's calculation of Cu bands including a linear cutoff at large \bar{k} , is shown in Fig.2-5.

To summarize, with explicit orthogonalization between the conduction band states and the d-band states, the OPW-OPW block can be expressed in the form

$$\begin{aligned} H_{\vec{k}_\nu, \vec{k}_\nu'} &= \langle \vec{k}_\nu | H | \vec{k}_\nu' \rangle \\ &= C_{\vec{k}_\nu}^{-1} C_{\vec{k}_\nu'}^{-1} [H^I + H^{II} + H^{III} + H^{IV}] \\ &= C_{\vec{k}_\nu}^{-1} C_{\vec{k}_\nu'}^{-1} [H^I + H^V - H^{IV}] \end{aligned} \quad (2.43)$$

with

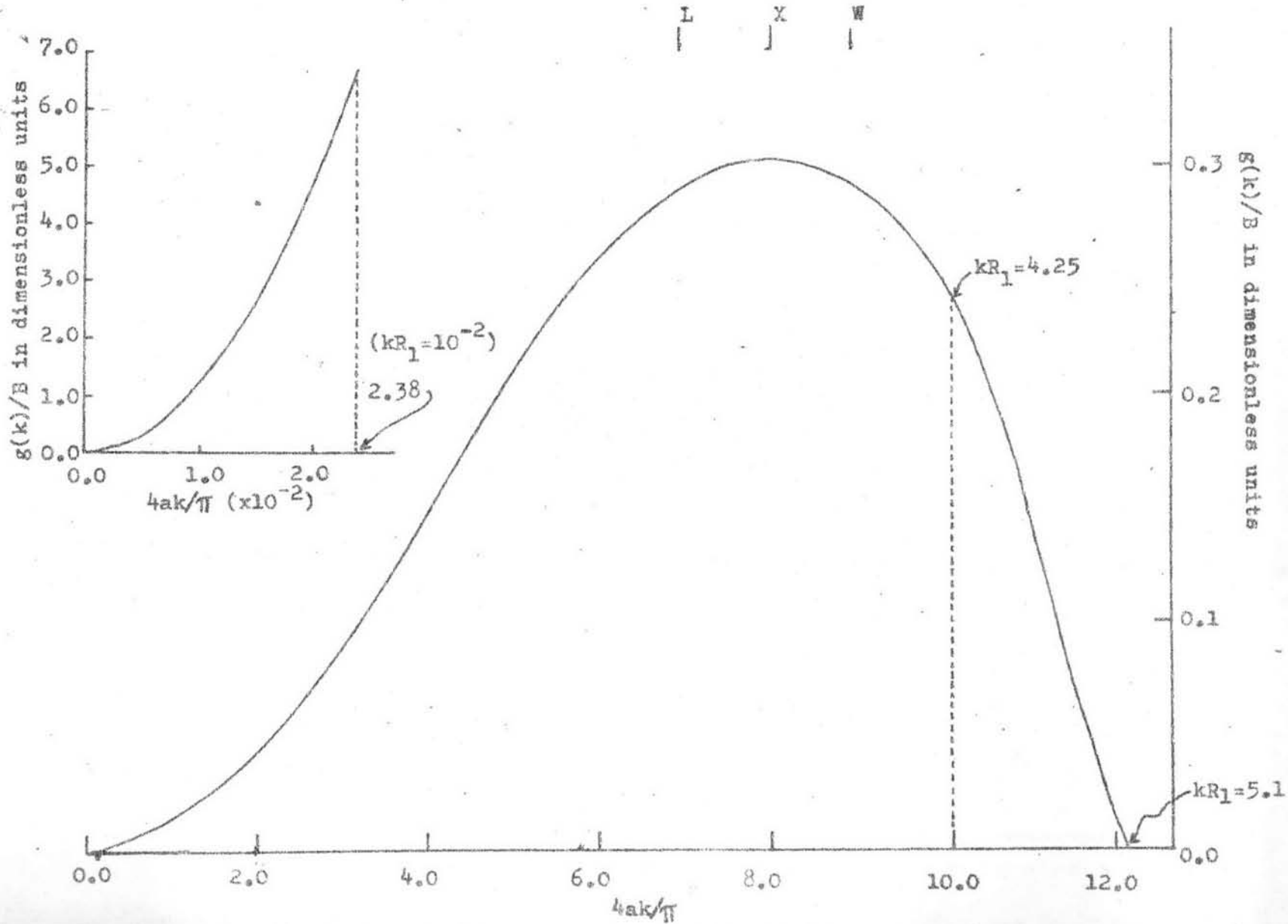
$$H^I = [\alpha |\vec{k} + \vec{k}_\nu|^2 + \beta] \delta_{\vec{k}_\nu, \vec{k}_\nu'} + \frac{V_{\vec{k}_\nu - \vec{k}_\nu'}}{K_\nu - K_{\nu'}} (1 - \delta_{\vec{k}_\nu, \vec{k}_\nu'}) \quad (2.44)$$

$$\begin{aligned} H^V &= - \sum_n C_n C_{n'} F_n(\vec{k}_\nu) F_{n'}(\vec{k}_\nu') \left(C_{\vec{k}_\nu} g(k_\nu) f(k_\nu') \right. \\ &\quad \left. + C_{\vec{k}_\nu'} g(k_\nu') f(k_\nu) \right) \end{aligned} \quad (2.45)$$

$$H^{IV} = \sum_{n, n'} C_n C_{n'} F_n(\vec{k}_\nu) F_{n'}(\vec{k}_\nu') f(k_\nu) f(k_\nu') H_{nn'} \quad (2.46)$$

Figure 2-5

The hybridization form factor $g(k)$ with a linear cutoff from kR_1 . The insert shows its values at region of small k . This is also the value used to fit the Burdick's Cu bands. The explicit algebraic expression can be seen in Subroutine RG listed in Appendix C.



and

$$\begin{aligned}
 f(k_\nu) &= K_0 j_2(k_\nu R_0) \\
 g(k_\nu) &= K_1 j_2(k_\nu R_1) \\
 \left| \frac{C_{\vec{k}_\nu}}{k_\nu} \right|^2 &= 1 - \sum_n \left| M_n(\vec{k}_\nu) \right|^2 \\
 &= 1 - \sum_n \left| C_n F_n(\vec{k}_\nu) \right|^2 f^2(k_\nu) \\
 &= 1 - \frac{1}{3} f^2(k_\nu) \\
 &= 1 - \frac{1}{3} K_0^2 j_2^2(k_\nu R_0)
 \end{aligned} \tag{2.47}$$

C_n and F_n are as shown in Eq.(2.11.A), and H_{nn} are as shown in Eq.(2.29). The simplified Eq.(2.43) is the starting equation for calculating all matrix elements of the OPW-OPW block of the Mueller's interpolation scheme. From this expression, one can see that the matrix elements of this block are quite complicated, each involving a number of the following adjustable parameters :

$$\alpha, \beta, V_{111}, V_{200}, K_0, R_0, K_1, R_1 .$$

Some further refinements are necessary for an effectively functioning interpolation scheme. If the orthogonalization effect has been neglected, or taken into account only through the parameters α , V_{111} , and V_{200} as described by Hodges, then

$$H^{IV} = 0, \quad H^V = 0, \quad \text{and} \quad C_{\vec{k}}^{-1} = 1 .$$



Then the explicit form of the OPW-OPW block becomes

$$\begin{bmatrix} H_{\vec{k}, \vec{k}'} \\ \vec{k}, \vec{k}' \end{bmatrix} = \begin{bmatrix} \beta + \alpha |\vec{k}|^2 & V_{200} & V_{111} & V_{111} \\ V_{200} & \beta + \alpha |\vec{k} + \vec{K}_2|^2 & V_{111} & V_{111} \\ V_{111} & V_{111} & \beta + \alpha |\vec{k} + \vec{K}_3|^2 & V_{200} \\ V_{111} & V_{111} & V_{200} & \beta + \alpha |\vec{k} + \vec{K}_4|^2 \end{bmatrix} \quad (2.48)$$

This has the same form as that used by Harrison²⁰ for the conduction bands of Al. The diagonal matrix elements correspond to a band having a simple parabolic form. β is a constant fixing the zero of energy. The real crystal potential is represented by the two pseudopotential Fourier coefficients V_{111} and V_{200} .

In transition metals and noble metals, V_{111} and V_{200} have fairly large values. It is then necessary to ensure the occurrence of properly symmetrized combinations of OPW's along symmetry directions. For example, at Γ the only symmetrized plane waves that can be formed using the \vec{K} vectors of Eq.(2.18) is $e^{i\vec{k} \cdot \vec{r}} = 1$ (involving only \vec{K}_1), corresponding to Γ_1 . The other plane waves, involving \vec{K}_2 , \vec{K}_3 , and \vec{K}_4 , appear in connection with other points in the Brillouin zone. The matrix in Eq.(2.48) allows undesirable wave function components \vec{K}_1 to occur at points of high symmetry. For instance, whereas the point X should involve only \vec{K}_1 and \vec{K}_2 , in its present form Eq.(2.48) also

involves \vec{K}_3 and \vec{K}_4 . These components must be suppressed. Hodges accomplished this by introducing arbitrary symmetrizing factors $F_{\vec{K}_\nu}(\vec{k})$ into the OPW-OPW matrix elements of Eq.(2.48). There are three distinct factors denoted by the \vec{K} vectors; namely $F_{0\bar{2}0}(\vec{k})$, $F_{\bar{1}\bar{1}\bar{1}}(\vec{k})$, and $F_{\bar{1}\bar{1}1}(\vec{k})$. They have values of 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. They should also vary their values smoothly between the symmetry points in the Brillouin zone. For the fcc lattices, the necessary values for the F's at high symmetry points are shown in Table 2-1.

Table 2-1 Values of symmetrizing factors $F_{\vec{K}_\nu}(\vec{k})$ at various symmetry points.

	$F_{0\bar{2}0}$	$F_{\bar{1}\bar{1}\bar{1}}$	$F_{\bar{1}\bar{1}1}$
$\Gamma(000)$	0	0	0
X(080)	1	0	0
L(444)	0	1	0
K(660)	0	1	1
W(480)	1	1	1
U(282)	1	1	0

$$\text{all } F_{(000)}(\vec{k}) = 1$$

While it is desirable to have a smooth variation of the F 's between symmetry points, its precise expression is not important. There have been many workable prescriptions, such as those used by Hodges²³. In our work, we use the following expressions :

$$\begin{aligned}
 F_{0\bar{2}0}(\vec{k}) &= \left[\sin \frac{\pi(k_y - k_x)}{2(16 - k_x - k_y)} \right]^2, \\
 F_{\bar{1}\bar{1}\bar{1}}(\vec{k}) &= \left[\sin \frac{\pi(k_x + k_z)}{2(12 - k_x)} \right]^2, \\
 F_{\bar{1}\bar{1}1}(\vec{k}) &= \left[\sin \frac{\pi(k_x - k_z)}{2(12 - k_y)} \right]^2.
 \end{aligned} \tag{2.49}$$

The matrix elements of the OPW-OPW block, including the symmetrizing factors $F_{\vec{k}}(\vec{k})$, for the fcc lattice, are shown below :

$$H_{\vec{k}_\nu \vec{k}_{\nu'}} = \begin{bmatrix}
 \beta + \alpha |\vec{k}|^2 & V_{200}^{F0\bar{2}0} & V_{111}^{F\bar{1}\bar{1}\bar{1}} & V_{111}^{F\bar{1}\bar{1}1} \\
 V_{200}^{F0\bar{2}0} & \beta + \alpha |\vec{k} + \vec{K}_2|^2 & V_{111}^{F0\bar{2}0} F_{\bar{1}\bar{1}\bar{1}} & V_{111}^{F0\bar{2}0} F_{\bar{1}\bar{1}1} \\
 V_{111}^{F\bar{1}\bar{1}\bar{1}} & V_{111}^{F0\bar{2}0} F_{\bar{1}\bar{1}\bar{1}} & \beta + \alpha |\vec{k} + \vec{K}_3|^2 & V_{200}^{F\bar{1}\bar{1}\bar{1}} F_{\bar{1}\bar{1}1} \\
 V_{111}^{F\bar{1}\bar{1}1} & V_{111}^{F0\bar{2}0} F_{\bar{1}\bar{1}1} & V_{200}^{F\bar{1}\bar{1}\bar{1}} F_{\bar{1}\bar{1}1} & \beta + \alpha |\vec{k} + \vec{K}_4|^2
 \end{bmatrix} \tag{2.50}$$

²³ L. Hodges and H. Ehrenreich, *Methods in Computational Physics*, edited by Berni Alder, Sidney Fernbach, and Manuel Rotenberg, V.8, p.149-190, 1968.

The omission of these symmetrizing factors would result in small but undesirable energy splittings and shifts of the order of the average deviation of the interpolated bands from those of first-principles band calculations according to our calculation.

5 The OPW-LCAO Block

The matrix elements in this block can be obtained from $\langle \vec{k}\nu | H | \vec{k}\nu' \rangle$ for $\nu = 1, 2, 3, 4$ labelling the 4 OPW's and $\nu' = 5, 6, 7, 8, 9$ labelling the 5 LCAO's. The matrix elements are therefore given by (2.38)

$$\langle n | H | \vec{k}\nu \rangle = C_n F_n(\vec{k}_\nu) g(k_\nu) \quad , \quad \nu = 1, \dots, 4$$

with C_n , F_n given by (2.11.A) and $g(k_\nu)$ by (2.42)

$$g(k_\nu) = K_1 j_2(k_\nu R_1) \quad .$$

For given \vec{K} vectors, the matrix elements are

$$\begin{aligned} H_{\nu 5} &= C_5 F_5(\vec{k}_\nu) g(k_\nu) = \frac{k_{\nu x} k_{\nu y}}{k_\nu^2} K_1 j_2(k_\nu R_1) \\ H_{\nu 6} &= C_6 F_6(\vec{k}_\nu) g(k_\nu) = \frac{k_{\nu y} k_{\nu z}}{k_\nu^2} K_1 j_2(k_\nu R_1) \\ H_{\nu 7} &= C_7 F_7(\vec{k}_\nu) g(k_\nu) = \frac{k_{\nu z} k_{\nu x}}{k_\nu^2} K_1 j_2(k_\nu R_1) \quad (2.52) \\ H_{\nu 8} &= C_8 F_8(\vec{k}_\nu) g(k_\nu) = \frac{1}{2} \left[\frac{k_{\nu x}^2}{k_\nu^2} - \frac{k_{\nu y}^2}{k_\nu^2} \right] K_1 j_2(k_\nu R_1) \\ H_{\nu 9} &= C_9 F_9(\vec{k}_\nu) g(k_\nu) = \frac{1}{2\sqrt{3}} \left[3 \frac{k_{\nu z}^2}{k_\nu^2} - 1 \right] K_1 j_2(k_\nu R_1) \quad . \end{aligned}$$

It is instructive, however, to examine the argument used by Hodges. Writing out the integral (2.38) explicitly, and using the atomic potential $V(\vec{r})$ as given in (2.26), we have

$$\begin{aligned}
 \langle n | H | \vec{k}_\nu \rangle &= (Nv_a)^{-\frac{1}{2}} \int e^{-i(\vec{k}+\vec{K}_\nu) \cdot \vec{r}} \left[\frac{p^2}{2m} + V(\vec{r}) \right] \\
 &\quad \times (N)^{-\frac{1}{2}} \sum_{\ell} e^{i\vec{k} \cdot \vec{R}_\ell} \varphi_n(\vec{r}-\vec{R}_\ell) d\vec{r} \\
 &= v_a^{-\frac{1}{2}} \int e^{-i(\vec{k}+\vec{K}_\nu) \cdot \vec{r}} \left[\frac{p^2}{2m} + U(\vec{r}) + \sum_{\ell \neq 0} U(\vec{r}-\vec{R}_\ell) \right] \varphi_n(\vec{r}) d\vec{r} \\
 &= v_a^{-\frac{1}{2}} \int e^{-i(\vec{k}+\vec{K}_\nu) \cdot \vec{r}} \left[E_{\text{atomic}} + \sum_{\ell \neq 0} U(\vec{r}-\vec{R}_\ell) \right] \varphi_n(\vec{r}) d\vec{r} .
 \end{aligned}
 \tag{2.53}$$

It was then assumed that the main contribution to the second integral comes from the region near a cell boundary where there exists maximum overlap between potential and wave function and $\sum_{\ell \neq 0} U(\vec{r}-\vec{R}_\ell)$ was approximated by a constant value \bar{U} , so that

$$\langle n | H | \vec{k}_\nu \rangle = (\bar{U} + E_{\text{atomic}}) (v_a)^{-\frac{1}{2}} \int e^{-i(\vec{k}+\vec{K}_\nu) \cdot \vec{r}} \varphi_n(\vec{r}) d\vec{r} .
 \tag{2.54}$$

By expanding the exponential factor in the spherical harmonics and spherical Bessel functions, and by noting that only the term $\ell = 2$ contributes to the integral, the radial part may be reduced to the parametrized form

$$\int_0^\infty j_2(k_\nu r) r^2 f(r) dr \propto j_2(k_\nu R_1) .
 \tag{2.55}$$

The integral was evaluated on the assumption that $r^2 f(r)$ is strongly peaked at $r = R_1$

The constant factors ($\bar{U} + E_{\text{atomic}}$) may be combined into other adjustable parameters. Since \bar{U} , or the average value for $\sum_{\ell \neq 0} U(\vec{r} - \vec{R}_\ell)$ at the cell boundary, may not be necessarily equal for the t_{2g} and e_g orbitals, two different adjustable parameters may be used, K_2 for the t_{2g} orbitals and K_3 for the e_g orbitals.

For the wave vectors

$$\vec{k}_\nu = \vec{k} + \vec{K}_\nu$$

the final parametrized forms of the matrix elements including the symmetrizing factors $F_{\vec{K}_\nu}(\vec{k})$ are

$$\begin{aligned} H_{\nu 5} &= K_2 j_2(k_\nu R_1) \frac{k_{\nu x} k_{\nu y}}{k_\nu^2} F_{\vec{K}_\nu}(\vec{k}) , \\ H_{\nu 6} &= K_2 j_2(k_\nu R_1) \frac{k_{\nu y} k_{\nu z}}{k_\nu^2} F_{\vec{K}_\nu}(\vec{k}) , \\ H_{\nu 7} &= K_2 j_2(k_\nu R_1) \frac{k_{\nu z} k_{\nu x}}{k_\nu^2} F_{\vec{K}_\nu}(\vec{k}) , \\ H_{\nu 8} &= K_3 j_2(k_\nu R_1) \frac{1}{2} \left[\frac{k_{\nu x}^2}{k_\nu^2} - \frac{k_{\nu y}^2}{k_\nu^2} \right] F_{\vec{K}_\nu}(\vec{k}) , \\ H_{\nu 9} &= K_3 j_2(k_\nu R_1) \frac{1}{2\sqrt{3}} \left[3 \frac{k_{\nu z}^2}{k_\nu^2} - 1 \right] F_{\vec{K}_\nu}(\vec{k}) . \end{aligned} \quad (2.56)$$

In our interpolation scheme, the parametrized form (2.56), rather than that of (2.52), are used. The symmetrizing factors $F_{\vec{K}}(\vec{k})$ are again introduced for the same reason as those explained in connection with the OPW-OPW matrix elements of (2.50). The introduction of two adjustable parameters K_2 and K_3 for the two different symmetries of d-orbitals in the cubic environment amounts to some relaxation of the d-isotropy ansatz introduced by Mueller. We have found that this allows for some improvement in the accuracy of our interpolation scheme. Our result for fitting the energy bands of Burdick's calculations for Cu will be discussed later in Chapter 4.

6 Summary of Parameters

Our interpolation scheme is a hybrid incorporating features from both Hodges' and Mueller's schemes in what we hope to be an optimum manner. This hybrid scheme involves a maximum of 17 parameters. Of these, 8 appear only in the secular matrix of the LCAO-LCAO block; namely E_0 , which is determined more or less by the lowest atomic d-levels, Δ , which is determined by the crystal field splitting, and A_1, \dots, A_6 , which are determined by the extent of the overlap between nearest-neighbors in the fcc lattice. Appearing only in the OPW-OPW block are the 6 parameters α , β , V_{111} , V_{200} , K_0 , and R_0 . α , which is allowed to be adjustable in Hodges' scheme, is held fixed at the value $\left[\frac{\hbar^2}{2m} \left(\frac{\pi}{4a} \right)^2 \right]$ in our hybrid scheme as in Mueller's scheme. This is to permit additional expression of the effect of the orthogonalization required for the conduction band states and the core 3d states. β , which is the average of the potential over the crystal, is fixed as the zero of the energy scale. V_{111} and V_{200} are the only Fourier coefficients of the pseudopotential connected by the 4 reciprocal lattice vectors employed in the 4-OPW approximation. K_0 and R_0 are parameters which account for the main part of the orthogonalization effects. The remaining parameters take care of the hybridization effects in the OPW-LCAO block; namely K_1 and R_1 . K_1 is replaced by two parameters, K_2 and K_3 if \bar{U} is allowed to have two distinct values for the t_{2g} and e_g symmetries of the d-orbitals.