

CHAPTER IV

TOTAL BAND STRUCTURE ENERGY OF TRANSITION METALS

This chapter is concerned with the application of Hubbard's theory described in the previous chapter to the calculation of the total band structure energy for transition metals.

Since much of this chapter deals with mathematical manipulations of Hubbard's theory, i.e. the transformation of the KKR-Z equation to a hybrid form, it may be more convenient to present the derivation after a summarization of the important results of the theory employed.

Hubbard's theory is based on the KKR-Z equation

$$\det \left| \left(\frac{\hbar^2 k_{nn}^2}{2m} - E \right) \delta_{nn'} + \Gamma_{nn'} \right| = 0 \quad \dots 1)$$

where the pseudopotential matrix elements of the KKR-Z equation are rearranged into the generalized Slater form, i.e.

$$\Gamma_{nn'} = \frac{4\pi}{c} \sum_l (2l+1) r_l^2 \gamma_l(r_l) j_l(k_n r_l) j_l(k_{n'} r_l) P_l(\cos \theta_{nn'}) \dots 2)$$

Here $\underline{k}_{nn} = \underline{K}_n + \underline{k}$; \underline{K}_n are reciprocal lattice vectors and \underline{k} is the wave propagation vector. E denotes the band energies for a crystal which are measured relative to the zero of the muffin-tin potential and l the orbital angular momentum. r_l defines an arbitrary radius chosen for a particular l and $0 < r_l < r_i$. $\theta_{nn'}$ denotes the angle between \underline{k}_{nn} and $\underline{k}_{n'}$. The function γ_l is defined through

$$\delta_1(r_1, \kappa) = - \frac{\tan \eta_1(\kappa)}{\kappa r_1^2 j_1(\kappa r_1) [j_1(\kappa r_1) - \tan \eta_1(\kappa) n_1(\kappa r_1)]} \dots 3)$$

where η_1 are the phase shifts of the l-partial waves scattered off the muffin-tin potential, j_1 and n_1 are spherical Bessel and Neumann functions respectively. r_1 are chosen according to the Pendry prescription²⁷ to avoid the zeroes of the bracket contained in the denominator of eq. 3). For $l=0$, r_1 is found to be different from r_i and for $l = 1, 2$ r_1 is set equal to r_i . In the case of $l=2$, $\tan \eta_1(\kappa)$ has a narrow resonance at the resonance energy, denoted by E_{d-res} , and hence δ_2 has a corresponding narrow infinity in the neighbourhood of E_{d-res} . On the basis of this argument δ_1 is written as

$$\delta_1 = \delta_1' - \delta_{1\lambda} \frac{\Gamma}{E_0 - E} \dots 4)$$

where E_0 and Γ are, respectively, the position and the width of the λ scattering resonance in δ_1 and δ_1' is a smooth residual part of δ_1 after the subtraction of the resonance contribution. It will be apparent later that the value of E_0 is not exactly equal to E_{d-res} .

To obtain the analytical expressions for the total band structure energy, we express the formulae for δ_1' , Γ and E_0 as functions of the energy E .

For $l=0$ and 1 cases, δ_1' has the same value as δ_1 since there are no resonances in δ_0 and δ_1 . Thus we obtain

$$\delta_1 = \delta_1' = \frac{\tan \eta_1(\kappa)}{\kappa r_1^2 j_1(\kappa r_1) [j_1(\kappa r_1) - \tan \eta_1(\kappa) n_1(\kappa r_1)]} \dots 5)$$

For the $l = 2$ case, we must take into account the resonance behaviour of the phase shift, i.e.

$$\tan \eta_l; \text{ near resonance} = \frac{W}{2 [E_{d\text{-res}} - E]} \dots 6)$$

where W is the width of resonance of $\tan \eta_l$, near the resonance energy $E_{d\text{-res}}$. For a resonance state we write

$$\tan \eta_\lambda = \tan \eta_\lambda^S(\kappa) + \frac{W}{2 [E_{d\text{-res}} - E]} \dots 7)$$

where $\eta_\lambda^S(\kappa)$ is a smooth residual phase shift. The substitution of eq. 7) into eq. 3) gives

$$\delta_\lambda = \frac{-\tan \eta_\lambda^S(\kappa) - \frac{W}{2 [E_{d\text{-res}} - E]}}{\kappa r_\lambda^2 j_\lambda(\kappa r_\lambda) \left[j_\lambda(\kappa r_\lambda) - \left\{ \tan \eta_\lambda^S(\kappa) + \frac{W}{2 [E_{d\text{-res}} - E]} \right\} n_\lambda(\kappa r_\lambda) \right]}$$

$$\delta_\lambda = \frac{[-2\{E_{d\text{-res}} - E\} \tan \eta_\lambda^S(\kappa) - W]}{\kappa r_\lambda^2 j_\lambda(\kappa r_\lambda) [j_\lambda(\kappa r_\lambda) - \tan \eta_\lambda^S(\kappa) n_\lambda(\kappa r_\lambda)]}$$

$$\delta_\lambda = \frac{1}{\left[2(E_{d\text{-res}} - E) - \frac{W n_\lambda(\kappa r_\lambda)}{\{j_\lambda(\kappa r_\lambda) - \tan \eta_\lambda^S(\kappa) n_\lambda(\kappa r_\lambda)\}} \right]}$$

Let us define

$$E_0(E) = E_{d-res} - \frac{W n_\lambda(\kappa r_\lambda)}{2 [j_\lambda(\kappa r_\lambda) - \tan \eta_\lambda^S(\kappa) n_\lambda(\kappa r_\lambda)]} \dots 9)$$

Then eq. 8) becomes

$$\begin{aligned} \gamma_\lambda &= \frac{-2 \left[\left\{ E_0 + \frac{W n_\lambda(\kappa r_\lambda)}{2 [j_\lambda(\kappa r_\lambda) - \tan \eta_\lambda^S(\kappa) n_\lambda(\kappa r_\lambda)]} - E \right\} + \frac{W}{2 \tan \eta_\lambda^S(\kappa)} \right] \tan \eta_\lambda^S(\kappa)}{2 \left[\kappa r_\lambda^2 j_\lambda(\kappa r_\lambda) \{ j_\lambda(\kappa r_\lambda) - \tan \eta_\lambda^S(\kappa) n_\lambda(\kappa r_\lambda) \} \right] [E_0 - E]} \\ &= \frac{-(E_0 - E) \tan \eta_\lambda^S(\kappa) - \frac{W}{2} \left[\frac{n_\lambda(\kappa r_\lambda) \tan \eta_\lambda^S(\kappa)}{j_\lambda(\kappa r_\lambda) - \tan \eta_\lambda^S(\kappa) n_\lambda(\kappa r_\lambda)} + 1 \right]}{\kappa r_\lambda^2 j_\lambda(\kappa r_\lambda) \{ j_\lambda(\kappa r_\lambda) - \tan \eta_\lambda^S(\kappa) n_\lambda(\kappa r_\lambda) \} (E_0 - E)} \\ &= \frac{-(E_0 - E) \tan \eta_\lambda^S(\kappa) - \frac{W}{2} \left[\frac{j_\lambda(\kappa r_\lambda)}{j_\lambda(\kappa r_\lambda) - \tan \eta_\lambda^S(\kappa) n_\lambda(\kappa r_\lambda)} \right]}{\kappa r_\lambda^2 j_\lambda(\kappa r_\lambda) \{ j_\lambda(\kappa r_\lambda) - \tan \eta_\lambda^S(\kappa) n_\lambda(\kappa r_\lambda) \} (E_0 - E)} \\ &= \frac{\tan \eta_\lambda^S(\kappa)}{\kappa r_\lambda^2 j_\lambda(\kappa r_\lambda) [j_\lambda(\kappa r_\lambda) - \tan \eta_\lambda^S(\kappa) n_\lambda(\kappa r_\lambda)]} \\ &= \frac{W}{2(E_0 - E) \kappa r_\lambda^2 [j_\lambda(\kappa r_\lambda) - \tan \eta_\lambda^S(\kappa) n_\lambda(\kappa r_\lambda)]^2} \\ \gamma_\lambda &= \gamma'_\lambda - \frac{\Gamma}{E_0(E) - E} \dots 10) \end{aligned}$$

where

$$\gamma'_\lambda = \frac{\tan \eta_\lambda^S(\kappa)}{\kappa r_\lambda^2 j_\lambda(\kappa r_\lambda) \left[j_\lambda(\kappa r_\lambda) - \tan \eta_\lambda^S(\kappa) n_\lambda(\kappa r_\lambda) \right]} \quad \dots 11)$$

and

$$\Gamma^3(E) = \frac{W}{2\kappa r_\lambda^2 \left[j_\lambda(\kappa r_\lambda) - \tan \eta_\lambda^S(\kappa) n_\lambda(\kappa r_\lambda) \right]^2} \quad \dots 12)$$

Now we can write the general formula of γ'_1 as given by eq. 4), by combining eqs. 5) and 10). γ'_λ and γ'_1 are of the same form except we have to replace the phase shift η_1 by the residual phase shift $\eta_\lambda^S(\kappa)$ for γ'_λ .

If we keep for γ'_1 only the first order term in $\tan \eta_1$, we write

$$\gamma'_1 = - \frac{\tan \eta_1(\kappa)}{\kappa r_1^2 j_1^2(\kappa r_1)} \quad \dots 13)$$

At very low energies we may approximate

$$\tan \eta_1 \sim \eta_1 \sim \frac{+(\kappa r_1)^{2l+1}}{(2l+1)!!(2l-1)!!} \quad \dots 14)$$

which is valid for an attractive potential. This result is obtained from a study of the behaviour of partial waves as a function of energies and is valid for $\kappa r_1 \ll 1$ and $\kappa r_0 \ll 1$ in the case of $l = 0$.
Substituting eq. 14) into eq. 13), we get

²⁸ A. Messiah, Quantum Mechanics (North-Holland Publishing Company), I, 391.

$$\gamma_1' = - \frac{r_1^{2l} r_1^{2l-1}}{(2l+1)!!(2l-1)!! j_1^2(kr_\lambda)} \dots 15)$$

As described in the previous chapter, Hubbard's theory yields a hybrid secular equation of the form

$$\det \begin{vmatrix} K' & h \\ h^* & A' \end{vmatrix} = 0 \dots 16)$$

where

$$K' = K + V - EI, \dots 17)$$

$$A' = A - EI. \dots 18)$$

K' , A' and h are matrices representing the conduction bands, the d-bands, and the hybridization between them. Their matrix elements are given by

$$K'_{nn'} = (k_n^2 - E) \delta_{nn'} + V_{nn'}, \dots 19)$$

$$A'_{mm'} = A_{mm'} - E \delta_{mm'}, \dots 20)$$

$$h_{nm} = -4\pi r_\lambda \left[\frac{r_1}{r} \right]^{1/2} j_\lambda(k_n r_\lambda) Y_{\lambda m}(\hat{k}_n) \dots 21)$$

where

$$V_{nn'} = \frac{4\pi}{\tau} \sum_l (2l+1) r_1^{2l} \gamma_l' j_l(k_n r_1) j_l(k_n r_1) P_l(\cos \theta_{nn'}), \dots 22)$$

$$A_{mm'} = E_0 \delta_{mm'} - (4\pi r_\lambda)^2 \sum_n^{(R)} \frac{\tau}{\tau} \frac{j_\lambda^2(k_n r_\lambda)}{k_n^2 - E} Y_{\lambda m}^*(\hat{k}_n) Y_{\lambda m}(\hat{k}_n) \dots 23)$$

All \underline{k}_n of eq. 16) belong to the preferred set P of the theory except those in the sum $\sum_n^{(R)}$ of eq. 23).

From eqs. 21), 20) and 23), it can be seen that Γ determines both the strength of the hybridization and the width or the shape of the d-bands. In the limit $\Gamma \rightarrow 0$, h vanishes and eq. 16) gives a set of d bands of zero width at $E = E_0$ which do not hybridize with the NFE bands. This limit will be taken as our zeroth model and we shall treat the corrections due to hybridization and d-band width to lowest order in Γ .

1. Hybridization and pseudopotential contributions to conduction bands

In this section we consider the effect of hybridization and the pseudopotential on the lowest free electron band when the resonance occurs at an energy within the lowest free electron band. If the resonance crosses the free electron band \underline{k}_n for some nonzero reciprocal lattice vector \underline{K}_n , then we replace \underline{k} by \underline{k}_n in the following.

First we write eq. 16) as

$$\det \begin{vmatrix} \underline{k}^2 + V_{00}(\underline{k}) - E & M \\ M^* & P \end{vmatrix} = 0 \quad \dots \quad 24)$$

where we have explicitly written the first diagonal term in the NFE block, assumed $V_{00}(\underline{k}_n)$ to be $V_{00}(\underline{k})$, and the matrices M and P denote the remaining elements of eq. 16). In order to obtain the effect of M and P on the lowest conduction band we follow the procedure

employed by Heine. A matrix transformation of eq. 24) gives

$$\det \begin{vmatrix} \underline{k}^2 + V_{00}(\underline{k}) - E & M \\ M^* & P \end{vmatrix} \begin{vmatrix} I & -\{\underline{k}^2 + V_{00}(\underline{k}) - E\} \\ -P^{-1}M^* & I \end{vmatrix} = 0,$$

$$\text{or } \det \begin{vmatrix} \underline{k}^2 + V_{00}(\underline{k}) - E - MP^{-1}M^* & 0 \\ 0 & P - M^*[\underline{k}^2 + V_{00}(\underline{k}) - E]^{-1}M \end{vmatrix} = 0. \quad \dots 25)$$

Consequently, the root corresponding to the lowest NFE band is contained in the equation

$$\underline{k}^2 + V_{00}(\underline{k}) - E - MP^{-1}M^* = 0$$

or

$$E = \underline{k}^2 + V_{00}(\underline{k}) - MP^{-1}M^* \quad \dots 26)$$

where the last term of eq. 26) is a function of energy E. Considering the last two terms on the right of eq. 26) to be small corrections to the free electron energy \underline{k}^2 , and keeping only contributions of order Γ and $|V|^2$ in $MP^{-1}M^*$, eq. 26) yields

$$E = \underline{k}^2 + V_{00}(\underline{k}) - \sum_{n \neq 0} \frac{|V_{0n}(\underline{k})|^2}{\underline{k}_n^2 - \underline{k}^2} - \sum_m \frac{|h_{0m}|^2}{E_0 - \underline{k}^2} \dots 27)$$

These lowest order terms can be obtained by inspection of eqs. 19)-23) by a) replacing E by \underline{k}^2 in $MP^{-1}M^*$; b) ignoring the last term on the right hand side of eq. 23) since it contributes to order Γ^2 and c) also ignoring the cross terms between V and h which contribute to order $\Gamma^{3/2}$. The third term on the right hand side of eq. 27) is

the familiar pseudopotential result of second order perturbation theory which is small in comparison with V_{00} . The last term is the hybridization correction to band \underline{k} . Let us denote eq. 27) by

$$E = E_{FE} + E_{pseu} + E_{\lambda} \quad \dots 28)$$

where

$$E_{FE} = \underline{k}^2 \quad \dots 29)$$

is the free electron energy contribution to band \underline{k} ,

$$E_{pseu} = V_{00}(\underline{k}) - \sum_{n \neq 0} \frac{|V_{On}(\underline{k})|^2}{\underline{k}_n^2 - \underline{k}^2} \quad \dots 30)$$

is the pseudopotential correction, and the lowest order correction due to the hybridization to the free electron energy, E_{λ} , is given by

$$E_{\lambda} = - \sum_m \frac{|h_{Om}(\underline{k})|^2}{E_0 - \underline{k}^2} \quad \dots 31)$$

According to eq. 13), 22) and 21), E_{pseu} vanishes if s, p phase shifts and the residual d phase shift vanish, and E_{λ} , the correction due to the presence of d-bands, vanishes as $\Gamma \rightarrow 0$.

2. The total energy of d-bands

The total energy of the d-bands of nonzero width without hybridization is obtained by summing the eigenvalues of the A' block of eq. 18). For each value of \underline{k} , the sum of the eigenvalues of the

matrix equals the trace of the matrix, so the total energy is

$$U_d = \frac{2}{N} \sum_{\underline{k} < \underline{k}_{\text{BZ}}} \sum_m (A'_{mm} + E) \quad \dots 32)$$

where $\underline{k}_{\text{BZ}}$ denotes a summation over all vectors \underline{k} in the reduced Brillouin zone, N is the number of atoms in the macroscopic crystal, and the factor 2 accounts for the two spin states corresponding to each \underline{k} value.

The substitution of eqs. 20) and 23) into eq. 32) gives

$$U_d = \frac{2}{N} \sum_{\underline{k} < \underline{k}_{\text{BZ}}} \sum_m \left[E_0 - (4\pi r_\lambda)^2 \sum_n^{(R)} \frac{\Gamma}{\mathcal{C}} \left\{ \frac{j_\lambda^2(k_n r_\lambda)}{k_n^2 - E} Y_{\lambda m}^*(\hat{k}_n) Y_{\lambda m}(\hat{k}_n) \right\} \right]. \quad \dots 33)$$

For the lowest order estimate, we approximate E by E_0 in eq. 33) and write

$$\begin{aligned} U_d &= 2 \sum_m E_0 - \frac{2}{N} \sum_{\underline{k} < \underline{k}_{\text{BZ}}} \sum_m (4\pi r_\lambda)^2 \sum_n^{(R)} \frac{\Gamma}{\mathcal{C}} \frac{j_\lambda^2(k_n r_\lambda)}{k_n^2 - E_0} \left| Y_{\lambda m}(\hat{k}_n) \right|^2, \\ &= U_d^{(0)} + U_d^{(1)} \quad \dots 34) \end{aligned}$$

where the first contribution

$$U_d^{(0)} = 2 \sum_m E_0, \quad \dots 35)$$

may be interpreted as the zero-order contribution of the d-bands, and the second contribution is defined by

$$U_d^{(1)} = -\frac{2}{N} \sum_{\underline{k} < k_{BZ}} \sum_m (4\pi r_\lambda)^2 \sum_n^{(R)} \frac{\Gamma}{\mathcal{C}} \frac{j_\lambda^2(k_n r_\lambda)}{k_n^2 - E_0} |Y_{\lambda m}(\hat{k}_n)|^2. \quad \dots 36)$$

This is a shift in the mean position of the d bands as a result of the nonzero width of d bands.

Next, we have to take into account the total hybridization effect on d bands due to all of the free electron states of wave vectors \underline{k}_n belonging to the preferred set P.

It can be easily shown that the effect of a free electron state on d bands is equal but opposite to that of d bands on the free electron state. To show this we consider eq. 16) which is transformed into

$$\det \begin{vmatrix} K + V - EI - h[A - EI]^{-1}h^* & 0 \\ 0 & A - EI - h^*[K + V - EI]^{-1}h \end{vmatrix} = 0. \quad \dots 37)$$

Eq. 37) yields

$$K + V - EI - h[A - EI]^{-1}h^* = 0,$$

or

$$EI = K + V - h[A - EI]^{-1}h^* \quad \dots 38)$$

and

$$A - EI - h^*[K + V - EI]^{-1}h = 0,$$

or

$$EI = A - h^*[K + V - EI]^{-1}h. \quad \dots 39)$$

The last terms of eqs. 38) and 39) are the hybridization corrections to the conduction band and the d bands respectively. They are equal but opposite to each other in zero order approximation.



This is achieved by iterating E by $K + V$ and A respectively in eqs. 38) and 39); we get instead of eqs. 38) and 39)

$$EI = K + V - h[A - (K + V)]^{-1}h^*, \quad \dots 40)$$

$$EI = A - h^*[K + V - A]^{-1}h. \quad \dots 41)$$

Hence the hybridization correction due to the free electron state \underline{k}_n is obtained by putting $\underline{k} = \underline{k}_n$ in $-E_\lambda$ given in eq. 31). The total hybridization effect per atom on the energy of d bands is

$$\begin{aligned} U_d^{hy} &= \frac{2}{N} \sum_{\underline{k} < \underline{k}_{BZ}} \sum_n^{(P)} \sum_m \frac{|h_{nm}|^2}{E_0 - \underline{k}_n^2}, \\ &= \frac{2}{N} \sum_{\underline{k} < \underline{k}_{BZ}} \sum_m (4\pi r_\lambda)^2 \sum_n^{(P)} \frac{j_\lambda^2(k_n r_\lambda)}{E_0 - \underline{k}_n^2} \left| Y_{\lambda m}(k_n) \right|^2. \end{aligned} \quad \dots 42)$$

3. The total band structure energy for transition metals

Here we apply the result of the preceding sections to the calculation of the total band structure energy per atom for transition metals. Collecting all contributions to the energy per atom, we have

$$U_{Total} = \frac{2}{N} \sum_{\underline{k} < \underline{k}_F} (E_{FE} + E_{pseu} + E_\lambda) + U_d^{(0)} + U_d^{(1)} + U_d^{hy}$$

where \underline{k}_F^2 is the Fermi energy. This will be denoted by

$$U_{\text{Total}} = U_{\text{FE}} + U_{\text{pseu}} + U_{\lambda} + U_{\text{d}}^{(0)} + U_{\text{d}}^{(1)} + U_{\text{d}}^{\text{hy}} \quad \dots 43)$$

where

$$\left. \begin{aligned} U_{\text{FE}} &= \frac{2}{N} \sum_{\underline{k} < \underline{k}_{\text{F}}} E_{\text{FE}}, \\ U_{\text{pseu}} &= \frac{2}{N} \sum_{\underline{k} < \underline{k}_{\text{F}}} E_{\text{pseu}}, \\ U_{\lambda} &= \frac{2}{N} \sum_{\underline{k} < \underline{k}_{\text{F}}} E_{\lambda} \end{aligned} \right\} \quad \dots 44)$$

As a result, the total band structure energy consists of the free electron energy U_{FE} , the pseudopotential correction U_{pseu} , the zero-order contribution of d bands $U_{\text{d}}^{(0)}$, the contribution due to the non-zero width of d bands $U_{\text{d}}^{(1)}$, the hybridization effects on the free electron band and on the d bands, U_{λ} and U_{d}^{hy} .

4. Results

In the following paragraphs we shall give the approximate formulae for the various contributions when we may approximate the Fermi surface by a sphere. In other words, we have neglected the directional dependence of \underline{k} in the following. The justification of this approximation is given by Brooks ²⁹.

²⁹ H. Brooks, "Binding in Metals," Transactions of the Metallurgical Society of AIME, 227, 546-560(1963).

U_{FE}

The substitution of eq. 29) into eq. 44) yields free electron contribution

$$\begin{aligned}
 U_{FE} &= \frac{2}{N} \sum_{\underline{k} < \underline{k}_F} k^2, \\
 &= \frac{2}{N} \frac{V}{(2\pi)^3} \int_{k < k_F} k^2 \cdot 4\pi k^2 dk, \\
 &= \frac{2}{(2\pi)^3} \frac{V}{N} \cdot 4\pi \frac{k_F^5}{5},
 \end{aligned}$$

$$U_{FE} = \frac{3}{5} k_F^2, \quad \dots 45)$$

where we have replaced k_F^3 by the relation

$$k_F^3 = 3\pi^2 N/V. \quad \dots 46)$$

V is the total volume of crystal and k_F^2 is the Fermi energy.

U_{pseu}

The pseudopotential correction is obtained by making use of eqs. 15), 22), 30) and 44). Here we shall neglect the second order correction of the pseudopotential since it is small in comparison with the first order. Therefore we have

$$U_{pseu} = \frac{2}{N} \sum_{\underline{k} < \underline{k}_F} V_{00}(\underline{k}),$$

$$\begin{aligned}
U_{\text{pseu}} &= \frac{2}{N} \sum_{k < k_F} \frac{4\pi}{c} \sum_{l=1}^{\infty} (2l+1) r_1^2 j_l^2(kr_1), \\
&= \frac{2}{N} \sum_{k < k_F} \frac{4\pi}{c} \sum_{l=1}^{\infty} (2l+1) r_1^2 \left[- \frac{k^{2l} r_1^{2l+1}}{(2l+1)!!(2l-1)!! j_l^2(kr_1)} \right] j_l^2(kr_1), \\
&= - \frac{2}{N} \frac{V}{(2\pi)^3} \cdot \frac{4\pi}{c} \sum_{l=1}^{\infty} \frac{(2l+1) r_1^{2l+1}}{(2l+1)!!(2l-1)!!} \int_{k < k_F} k^{2l} \cdot 4\pi k^2 dk, \\
&= - \frac{4}{\pi} \sum_{l=1}^{\infty} \frac{r_1^{2l+1}}{\{(2l-1)!!\}^2 (2l+3)} k_F^{2l+3}, \\
&= - \frac{4}{\pi} k_F^3 \sum_{l=1}^{\infty} \frac{r_1^{2l+1}}{\{(2l-1)!!\}^2} \frac{k_F^{2l}}{(2l+3)}, \\
&= - \frac{4}{\pi} k_F^3 \left[\frac{r_0}{3} + \frac{r_1^3}{5} k_F^2 + \frac{r_2^5}{63} k_F^4 \right] \dots 47)
\end{aligned}$$

By introducing the radius of the Wigner Seitz cell, r_s , such that

$$V/N = (4/3)\pi r_s^3,$$

consequently

$$k_F^3 = \frac{3\pi^2}{(4/3)\pi r_s^3} = \frac{9\pi}{4r_s^3},$$

eq. 47) becomes

$$\begin{aligned}
U_{\text{pseu}} &= - \frac{4}{\pi} \frac{9\pi}{4r_s^3} \left[\frac{r_0}{3} + \frac{r_1^3}{5} k_F^2 + \frac{r_2^5}{63} k_F^4 \right], \\
U_{\text{pseu}} &= - \frac{3r_0}{r_s^3} - \frac{9}{5} \frac{r_1^3}{r_s^3} k_F^2 - \frac{1}{7} \frac{r_2^5}{r_s^3} k_F^4 \dots 48)
\end{aligned}$$

U_λ

In order to estimate the effect of d bands on the band k we now define the resonant energy E_0 as the value of E which causes the denominator in eq. 10) to become zero. That is $E_0 = E_0(E_0)$. According to this definition, the explicit energy dependence is now removed as a first approximation. Furthermore, it follows from eq. 12) that it is a good approximation to replace $\Gamma(E)$ by its resonant value, i.e.

$$\Gamma(E_0) = \frac{W}{2 \kappa_0^2 r_\lambda^2} \frac{1}{\left[j_\lambda(\kappa_0 r_\lambda) - \tan \eta_\lambda^B(\kappa_0) n_\lambda(\kappa_0 r_\lambda) \right]^2} \quad \dots \quad 49)$$

where $\kappa_0^2 = E_0$. The resonant constant W may be determined by locating the energy E_{d-res} at which $\tan \eta_1$ becomes infinite and W can be calculated from the formula

$$W = \lim_{E \rightarrow E_{d-res}} 2 \left[E_{d-res} - E \right] \tan \eta_1(E). \quad \dots \quad 50)$$

Hence $E_0(E)$ and $\Gamma(E)$ are now replaced by $E_0(E_0)$ and $\Gamma(E_0)$.

The effect of d bands on the band k is obtained by using eqs. 21), 31) and 44):

$$U_\lambda = \frac{2}{N} \sum_{\underline{k} < \underline{k}_F} \left\{ - \sum_m \frac{|h_{0m}(\underline{k})|^2}{E_0 - \underline{k}^2} \right\},$$

$$= - \frac{2}{N} \sum_{\underline{k} < \underline{k}_F} \sum_m (4\pi r_\lambda)^2 \frac{\Gamma}{\mathcal{C}} \frac{j_\lambda^2(\underline{k} r_\lambda)}{E_0 - \underline{k}^2} |Y_{\lambda m}(\hat{\underline{k}})|^2,$$

$$U_{\lambda} = - \frac{2}{N} (4\pi r_{\lambda})^2 \frac{\Gamma^{\lambda}(E_0) V}{\zeta (2\pi)^3} \sum_m \int_{k < k_F} \frac{j_{\lambda}^2(kr_{\lambda})}{E_0 - k^2} k^2 dk$$

$$\cdot \int_0^{2\pi} \int_0^{\pi} |Y_{\lambda m}(\hat{k})|^2 \sin \theta d\theta d\varphi \dots 51)$$

Assuming $j_{\lambda}(kr_{\lambda})$ changes slightly over the whole range of k , we substitute into eq. 51) the asymptotic behaviour

$$j_{\lambda}(kr_{\lambda}) \sim \frac{(kr_{\lambda})^{\lambda}}{(2\lambda+1)!!} \dots 52)$$

in order to obtain

$$U_{\lambda} = - \sum_m \frac{4\Gamma^{\lambda}(E_0)}{\pi} \frac{r_{\lambda}^{2\lambda}}{(2\lambda+1)!!} \int_{k < k_F} \frac{k^{2\lambda+2}}{E_0(E_0) - k^2} dk,$$

$$= - \frac{4\Gamma^{\lambda}(E_0)}{\pi} \frac{r_2^6}{225} \sum_m \left[\frac{\{E_0(E_0)\}^{3/2}}{2} \ln \frac{\sqrt{E_0(E_0)+k_F}}{\sqrt{E_0(E_0)-k_F}} \right.$$

$$\left. - \{E_0(E_0)\}^2 k_F - \frac{E_0(E_0)}{3} k_F^3 - k_F^5 \right] \dots 53)$$

where we have put $\lambda = 2$ for transition metals; the symbol λ for the orbital angular momentum of the resonant state and m for the magnetic quantum number, $-\lambda \leq m \leq \lambda$.

$$\underline{U_d^{(0)}}$$

The zero order contribution of the d-bands is given by eq. 35).

$$\underline{U_d^{(1)} + U_d^{hy}}$$

The sum of eqs. 36) and 42), i.e., the contribution due to the shift of the mean position of d bands and the hybridization correction to d bands, is

$$U_d^{(1)} + U_d^{hy} = -\frac{2}{N} \sum_{\underline{k} < \underline{k}_{BZ}} \sum_m (4\pi r_\lambda)^2 \frac{\Gamma(E_0)}{\tau} \sum_n^{(P+R)} \frac{j_\lambda^2(k_n r_\lambda)}{k_n^2 - E_0(E_0)} \cdot |Y_{\lambda m}(\hat{k}_n)|^2 \quad \dots 54)$$

Making use of the procedure recommended by Hubbard, we obtain, instead of eq. 54), the following,

$$U_d^{(1)} + U_d^{hy} = -\frac{2}{N} \sum_{\underline{k} < \underline{k}_{BZ}} (4\pi r_\lambda)^2 \frac{\Gamma(E_0)}{\tau} \left[\sum_n^{(P+S)} \frac{j_\lambda^2(k_n r_\lambda)}{k_n^2 - E_0(E_0)} |Y_{\lambda m}(\hat{k}_n)|^2 + \frac{1}{r_\lambda \tau_k} \left\{ \frac{1 - \cos X}{X} + \frac{\pi}{2} - \text{Si}(X) \right\} \right] \quad \dots 55)$$

$X = 2r_\lambda k_0$

where τ_k , k_0 and the vectors \underline{k}_n of P and S sets are defined in the previous chapter.

5. Summary and discussions

To summarize, what has been achieved for the present study is an approximate expression for the total band structure energy per atom for transition metals. Our results are based on the hybrid secular equation derived by Hubbard . The electronic energy bands of a

transition metal are represented as hybridizing nearly free electron bands and d bands. The width of the d scattering resonance in δ_1 of the muffin-tin potential, i.e. $|\Gamma|$, controls both the width and shape of d-bands and the strength of the hybridization between d bands and the NFE band. To calculate the total band structure energy, we sum one electron energies of all occupied free electron band and pure d-bands and take into account the hybridization and pseudopotential corrections which are consistently retained to lowest order terms in $|\Gamma|$ and the pseudopotential V .

The zeroth order of the total band structure energy per atom consists of contributions from a free electron band filled to a Fermi energy $E_F = k_F^2$ and from an occupied set of d bands of zero width at an energy $E_0(E_0)$, i.e. $U_{FE} + U_d^{(0)}$. Let us denote this part by U_0 ;

$$U_0 = U_{FE} + U_d^{(0)}. \quad \dots 56)$$

Replacing eqs. 45) and 35) into eq. 56), we obtain

$$U_0 = \frac{3}{5} k_F^2 + 2 \sum_m E_0(E_0). \quad \dots 57)$$

The first order corrections consist of U_{pseu} : pseudopotential effect, U_λ : hybridization effect on the free electron band, $U_d^{(1)}$: the shift of d bands due to their nonzero width, and U_d^{hy} : the hybridization effect on d bands due to the interaction with all free electron bands k_n of the preferred set P. Hence, calling the sum of these contributions U_1 , we have

$$U_1 = U_{\text{pseu}} + U_\lambda + (U_d^{(1)} + U_d^{\text{hy}}). \quad \dots 58)$$

Substituting eqs. 48), 53) and 55) into eq. 58),

$$\begin{aligned}
 U_1 = & -\frac{3r_0}{r_s^3} - \frac{9}{5} \frac{r_1^3}{r_s^3} k_F^2 - \frac{1}{7} \frac{r_2^5}{r_s^3} k_F^4 \\
 & - \left[\frac{4\pi(E_0)}{\pi} \frac{r_2^6}{225} \sum_m \left[\frac{\{E_0(E_0)\}^{3/2}}{2} \ln \frac{\sqrt{E_0(E_0)+k_F}}{\sqrt{E_0(E_0)-k_F}} \right. \right. \\
 & \left. \left. - \{E_0(E_0)\}^2 k_F - \frac{1}{3} E_0(E_0) k_F^3 - k_F^5 \right] \right] - \frac{2}{N} \sum_{k < k_{\text{BZ}}} (4\pi r_\lambda)^2 \frac{\pi(E_0)}{\tau} \\
 & \cdot \left[\sum_n^{(P+S)} \frac{j_\lambda^2(k_n r_\lambda)}{k_n^2 - E_0(E_0)} \left| Y_{\lambda m}^\lambda(k_n) \right|^2 + \frac{1}{r_\lambda \tau_k} \left\{ \frac{1 - \cos X}{X} + \frac{\pi}{2} - \text{Si}(X) \right\} \right] \cdot \\
 & \qquad \qquad \qquad X = 2r_\lambda k_0
 \end{aligned} \quad \dots 59)$$

These contributions are measured relative to the zero of the muffin-tin potential and $r_1 = r_2 = r_i$ because of Pendry's prescription of r_i .

The first term on the right of eq. 59), $-3r_0/r_s^3$, or the s-pseudopotential correction, affects the shift of the bottom of the conduction band relative to the muffin-tin zero. The second term, $(-9/5) \cdot (r_1^3/r_s^3)k_F^2$, or the p-pseudopotential correction, affects the kinetic energy of the free electron. The addition of this term to the zeroth order contribution of the conduction band gives

$$\frac{3}{5} k_F^2 - \frac{9}{5} \frac{r_1^3}{r_s^3} k_F^2 = \frac{3}{5} k_F^2 \left[1 - \frac{3r_1^3}{r_s^3} \right] \cdot \dots 60)$$

In other words, the effective mass of conduction electron is $\left[1 - \frac{3r_1^3}{r_s^3} \right]^{-1}$

instead of 1. The term of order k_F^4 is the nonresonant contribution of d-phase shift which is spherically symmetrical in \underline{k} -space. The terms in the first bracket of eq. 59), the hybridization effect of d-bands on the conduction band, affects the shift of the bottom of the band and gives asymmetrical fluctuation of the band structures. The rest of eq. 59) describes the effect of the shift of the positions of d bands and the hybridization interactions of d bands with all \underline{k}_n bands of the preferred set P. Now we may write the final result, instead of eq. 43), in the following manner:

$$U_{\text{Total}} = U_0 + U_1,$$

$$\begin{aligned}
 &= - \frac{3r_0}{r_s^3} + 2 \sum_m E_0 + \frac{3}{5} \left[1 - \frac{r_i^3}{r_s^3} \right] k_F^2 - \frac{1}{7} \frac{r_i^5}{r_s^5} k_F^4 \\
 &\quad - \frac{4\Gamma(E_0)}{\pi} \frac{r_2^6}{225} \sum_m \left[\frac{\{E_0(E_0)\}^{3/2}}{2} \ln \frac{\sqrt{E_0(E_0)+k_F}}{\sqrt{E_0(E_0)-k_F}} - \{E_0(E_0)\}^2 k_F \right. \\
 &\quad \left. - \frac{E_0(E_0)}{3} k_F^3 - k_F^5 \right] - \frac{2}{N} \sum_{k < k_{\text{BZ}}} (4\pi r_\lambda)^2 \frac{\Gamma(E_0)}{\tau} \\
 &\quad \cdot \left[\sum_n^{(P+S)} \frac{j_\lambda^2(k_n r_\lambda)}{k_n^2 - E_0(E_0)} \left| Y_{\lambda m}(k_n) \right|^2 + \frac{1}{r_\lambda \tau k} \left\{ \frac{1 - \cos X}{X} + \frac{\pi}{2} - \text{Si}(X) \right\} \right]. \\
 &\hspace{20em} X = 2r_\lambda k_0
 \end{aligned}$$

... 61)

$E_0(E_0)$ and $\Gamma(E_0)$ are the resonance constants. $E_0(E_0)$ is obtained as the zero of the denominator of eq. 10) and $\Gamma(E_0)$ is defined by eq. 49) with W given by eq. 50).

With the physical parameters $E_0(E_0)$ and $\Gamma(E_0)$ obtained from

these calculations and some other necessary parameters used, i.e. r_0, r_i , one can calculate the total energy using the present results.

In order to investigate the energy dependence of the present theory, we may, instead of eqs. 9) and 12), estimate E_0 by E_{d-res} and Γ by the lowest order term, i.e.

$$\Gamma \sim \frac{W}{2kr_\lambda^2 j_\lambda^2(kr_\lambda)} \sim \frac{W}{2kr_\lambda^2 j_\lambda^2(kr_\lambda)} \dots 62)$$

The substitution of this formula for Γ into eq. 44) together with the use of eqs. 31) and 21) yield the effects of d bands on the band

$$\begin{aligned} \underline{U}_\lambda &= \frac{2}{N} \sum_{\underline{k} < \underline{k}_F} E_\lambda, \\ &= - \frac{2}{N} \sum_{\underline{k} < \underline{k}_F} \sum_m \frac{|h_{0m}(\underline{k})|^2}{E_{d-res} - k^2}, \\ &= - \frac{2}{N} \sum_{\underline{k} < \underline{k}_F} \sum_m \frac{(-4\pi r_\lambda)^2}{E_{d-res} - k^2} \frac{\Gamma}{c} j_\lambda^2(kr_\lambda) |Y_{\lambda m}(\hat{k})|^2, \\ &= - \frac{2}{N} \frac{(4\pi r_\lambda)^2}{c} \frac{v}{(2\pi)^3} \sum_m \int_{k < k_F} \frac{W}{2kr_\lambda^2 j_\lambda^2(kr_\lambda)} \frac{j_\lambda^2(kr_\lambda)}{E_{d-res} - k^2} k^2 dk \\ &\quad \cdot \int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\varphi |Y_{\lambda m}(\hat{k})|^2, \\ &= - \frac{2W}{\pi} \sum_m \int_{k < k_F} \frac{k}{E_{d-res} - k^2} dk, \end{aligned}$$

$$\begin{aligned}
 U_{\lambda} &= \frac{W}{\pi} \sum_m \int_{k < k_F} \frac{1}{E_{d\text{-res}} - k^2} d(E_0 - k^2), \\
 &= \frac{W}{\pi} \sum_m \ln |E_{d\text{-res}} - E_F| / E_{d\text{-res}} \quad \dots 63)
 \end{aligned}$$

For a metal with filled d bands, our final result becomes

$$U_{\lambda} = \frac{5W}{\pi} \ln |E_{d\text{-res}} - E_F| / E_{d\text{-res}} \quad \dots 64)$$

This contribution is exactly the same as that of Deegan (Cf. eq. (4.13) of reference 30).

However the cancellation of $U_d^{(1)}$ and U_d^{hy} for the present theory is not as obvious as that of Deegan's. This is due to the different procedures employed in the theories.

6. Conclusions

This thesis is primarily concerned with a review of the basic concepts for band structure calculations. Some original articles on the first-principles methods for band structure calculations, namely the KKR and KKR-Z methods, are studied. The justification of the model Hamiltonian method or the interpolation scheme for transition metals achieved by Heine is also reviewed. The approximate hybrid scheme devised by Hubbard for transition metals is rederived with more mathematical detail. The framework of Hubbard's theory

³⁰ R.A. Deegan, "Total Energy of d-Band Metals: Alkaline-Earth and Noble Metals," Physical Review B, 186, 619-624(1969).

is adopted for a study of s-d hybridization and pseudopotential effects as well as the total band structure energy per atom in the iron series transition metals. For the present course of work, an approximate expression for the evaluation of the total band structure energy per atom based on the Hubbard theory is obtained by consistently retaining only the lowest order terms.

In comparison with the work of Deegan³⁰, which is based on another version of Hubbard's hybrid theory with an arbitrary cut off parameter¹¹, the present result may be regarded as being more general and thus physically more interesting as no arbitrary parameters are involved in the theory. Though, during the present course of work, no numerical calculation was attempted, this work should provide a great deal of physical understanding of the interpolation schemes. It is also possible to employ the present theory to investigate some other physical properties such as the compressibility of transition metals.

It is hoped that the present work will be substantiated by future investigation, perhaps, an investigation of our results numerically.

APPENDIX A

THE GREENIAN OF THE SYSTEM

In this appendix the alternative form of the Green's function defined by eq. 11) of chapter II is given. The present representation is useful for the derivation of the KKR-Z equation. The argument is as follows:

A Schrödinger equation such as

$$\left[-\nabla^2 + V(\underline{r}) - E(k) \right] \Psi(\underline{r}) = 0 \quad \dots 1)$$

may always be transformed²⁴ into a homogeneous integral equation

$$\Psi(\underline{r}) = \int_{\text{all space}} G_0(\underline{r}, \underline{r}') V(\underline{r}') \Psi(\underline{r}') d\underline{r}' \quad \dots 2)$$

for the wave function $\Psi(\underline{r})$ in any potential $V(\underline{r})$.

$$G_0(\underline{r}, \underline{r}') \equiv G_0(\underline{r} - \underline{r}') \equiv G_0(\underline{R}) \equiv -\frac{1}{4\pi} \frac{\exp(i\kappa|\underline{r} - \underline{r}'|)}{|\underline{r} - \underline{r}'|} \quad \dots 3)$$

is the free-particle propagator, or Green function at the energy $E = \kappa^2$.

The physical interpretation of eq. 2) is that the wave function is scattered by the potential into itself; the wavelets coming from all different points \underline{r}' with strength $V(\underline{r}') \Psi(\underline{r}')$ combine to give $\Psi(\underline{r})$ again. For simplicity the potential $V(\underline{r})$ is supposed to be of the muffin-tin form

$$V(\underline{r}) = \sum_{\underline{l}} U(\underline{r}-\underline{l}) \quad \dots 4)$$

where U is the atomic potential located at the lattice site \underline{l} ; \underline{l} is the actual position of the ion. For convenience, we have used the symbol \underline{l} instead of \underline{r}_S as in chapter II. Substituting eqs. 3) and 4) into eq. 2), we get

$$\Psi(\underline{r}) = -\frac{1}{4\pi} \sum_{\underline{l}'} \int \frac{\exp(i\kappa|\underline{r}-\underline{r}'|)}{|\underline{r}-\underline{r}'|} U(\underline{r}'-\underline{l}') \Psi(\underline{r}') d\tau' \quad \dots 5)$$

where the integral is over only the cell τ' around \underline{l}' , since $U(\underline{r}-\underline{l})$ vanishes elsewhere. Eq. 5) is really a sum of separate integrals since the muffin-tin spheres do not overlap as we may demonstrate by introducing a variable $\underline{\rho}$ such that $\underline{r} = \underline{l} + \underline{\rho}$ in the l th cell of the crystal. Thus

$$\Psi(\underline{l}+\underline{\rho}) = -\frac{1}{4\pi} \sum_{\underline{l}'} \int_{\text{cell}} \frac{\exp(i\kappa|\underline{l}+\underline{\rho}-\underline{l}'-\underline{\rho}'|)}{|\underline{l}+\underline{\rho}-\underline{l}'-\underline{\rho}'|} U(\underline{\rho}') \Psi(\underline{l}'+\underline{\rho}') d\tau'. \quad \dots 6)$$

Now we recall that Ψ is to be a Bloch function, i.e.,

$$\Psi(\underline{l}+\underline{\rho}) = \exp(i\kappa \cdot \underline{l}) \Psi(\underline{\rho}). \quad \dots 7)$$

Substituting eq. 7) into eq. 6), we get

$$\exp(i\kappa \cdot \underline{l}) \Psi(\underline{\rho}) = -\frac{1}{4\pi} \sum_{\underline{l}'} \int_{\text{cell}} \frac{\exp(i\kappa|\underline{\rho}-\underline{\rho}'+\underline{l}-\underline{l}'|)}{|\underline{\rho}-\underline{\rho}'+\underline{l}-\underline{l}'|} U(\underline{\rho}') \exp(i\kappa \cdot \underline{l}') \cdot \Psi(\underline{\rho}') d\tau',$$

$$\begin{aligned} \Psi(\underline{r}) &= - \frac{1}{4\pi} \sum_{\underline{l}'} \int_{\text{cell}} \left[\frac{\exp(i\kappa|\underline{r}-\underline{r}'+\underline{l}-\underline{l}'|) \exp\{-i\kappa \cdot (\underline{l}-\underline{l}')\}}{|\underline{r}-\underline{r}'+\underline{l}-\underline{l}'|} \right] u(\underline{r}') \\ &\quad \cdot \Psi(\underline{r}') d\tau', \\ &= \int_{\text{cell}} \left[\sum_{\underline{l}'} G_0(\underline{r}-\underline{r}'+\underline{l}-\underline{l}') \exp\{-i\kappa \cdot (\underline{l}-\underline{l}')\} \right] u(\underline{r}') \Psi(\underline{r}') d\tau', \\ \Psi(\underline{r}) &= \int_{\text{cell}} G_{\underline{k}}(\kappa, \underline{r}-\underline{r}') u(\underline{r}') \Psi(\underline{r}') d\tau' \quad \dots \quad 8) \end{aligned}$$

where

$$G_{\underline{k}}(\kappa, \underline{r}-\underline{r}') \equiv \sum_{\underline{l}'} G_0(\underline{r}-\underline{r}'+\underline{l}-\underline{l}') \exp\{-i\kappa \cdot (\underline{l}-\underline{l}')\}. \quad \dots \quad 9)$$

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This function is called the "complete Greenian" of the lattice which is central to the whole band structure problem. From the translational symmetry of the crystal, $G_{\underline{k}}$ obviously does not depend on the choice of \underline{l} , but is a function of two variables \underline{r} and \underline{r}' which may refer to points in the same unit cell. The significance of eq. 8) is that the whole crystal takes part in transforming the wave function into itself. In comparison with the Kohn-Rostoker formulation, the Green's function may be expressed as

$$G(\underline{r}, \underline{r}') = - \frac{1}{4\pi} \sum_{\underline{l}'} \frac{\exp(i\kappa|\underline{r}-\underline{r}'+\underline{l}-\underline{l}'|)}{|\underline{r}-\underline{r}'+\underline{l}-\underline{l}'|} \exp\{-i\kappa \cdot (\underline{l}-\underline{l}')\}.$$

Putting $\underline{l} = 0$, replacing \underline{l}' by \underline{l} and $\underline{r}-\underline{r}'$ by \underline{R} , we get

$$G(\underline{R}) = G(\underline{r}, \underline{r}') = - \frac{1}{4\pi} \sum_{\underline{l}} \frac{\exp(i\underline{k}|\underline{R}-\underline{l}|)}{|\underline{R}-\underline{l}|} \exp(i\underline{k}\cdot\underline{l}) \dots \dots 10)$$

This is the alternative form of the Green's function given in eq. 11) of chapter II.