

CHAPTER III

FIRST-PRINCIPLES DERIVATIONS OF THE INTERPOLATION SCHEMES FOR THE BAND STRUCTURES OF TRANSITION METALS

The success of the interpolation schemes for transition metals devised by Hodges et al.⁴ and by Mueller⁵ led one to investigate whether such schemes could be derived directly from first-principles calculations. Heine was the first who obtained a model Hamiltonian in a form which could be exhibited as a transformation of the fundamental Korringa-Kohn-Rostoker-Ziman (KKR-Z) formulation of the energy band problem. His derivation is not rigorous but physically motivated. After Heine's justification, Hubbard¹⁰ and Jacobs¹² have independently derived model Hamiltonian methods for the calculation of the electronic band structures of transition metals. Both techniques took as starting points the Korringa-Kohn-Rostoker (KKR) method. Not only was justification for such a model as an interpolation scheme achieved but also these derivations provided methods for first-principles calculations of energy bands. The work of Jacobs differed from that of Hubbard essentially in the choice of identities introduced for splitting the geometrical structure constants $A_{lm;l'm'}$ appearing in the KKR theory. The later work of Hum and Wong¹⁴ is based on the techniques developed by Jacobs and by Hubbard. The improved version of Hubbard's theory by Hubbard and Dalton¹¹ was further investigated by Pettifor¹³. All of these subsequent works are more formally based than that of Heine and these derivations can serve as approximate methods for band

structure calculations and they all have the simplicity of the interpolation schemes.

However, all of these derivations originated in the work of Heine and may be thought of as having two objectives (i) to explain the success of the interpolation schemes of Hodges et al. and of Mueller, (ii) to transform these interpolation schemes into a fast but approximate method for first-principles calculations of transition-metal band structures. All the improved schemes are attempted to provide a rapid first-principles method for the calculation of transition metal band structures and have been successful in objective (i) but not quite in objective (ii). Though they have succeeded in giving a fast method for calculating band structures, they suffer from defects which limit their general usefulness. The chief defects of these schemes are caused by the inclusion of an arbitrary parameter which was originally hoped to be insensitive in the calculations. In practice, it is found that the appropriate choice of the parameter is vital if good accuracy is to be obtained.

It seems quite impossible to estimate the parameter well enough to give the required accuracy to about 0.01 rydberg if band structures calculated by some other methods are not available for comparing the results. Even with a good choice of the parameter it is found that quite large secular equations are needed in order to obtain an accuracy of such an order. To avoid these difficulties a more suitable scheme is sought and as a result a new theory without

arbitrary parameter has been successfully developed by Hubbard ²² .

In this chapter, a physical description of the interpolation schemes based upon Heine's formulation will be sketched. Mathematical details will be suppressed as far as possible in order to stress the physical ideas. The interested reader may consult the original paper ⁹ . A description of Hubbard's theory without the arbitrary parameter is also given for we shall take advantage of this scheme in the study of the total band structure energy of transition metals. It may be helpful for the reader to understand the functional form of the pseudopotentials obtained by Heine if a general description of transition metal band structures is inserted here.

1. A general description of the band structures of pure transition metals

1.a) The transition from bound to free bands

To understand the formation of electronic energy bands in solids, an oversimplified picture of a formation of narrow tight-bound bands and nearly free electron bands is illustrated schematically in Fig. 5. The figure on the left shows the electronic states for a free-atom potential which is strong enough to bind all electrons that will later be free in the conduction band of the metal

²² J. Hubbard, "The Approximate calculation of Electronic Band Structures III," Journal of Physics C (Solid state physics), [2], 2, 1222-1229 (1969).

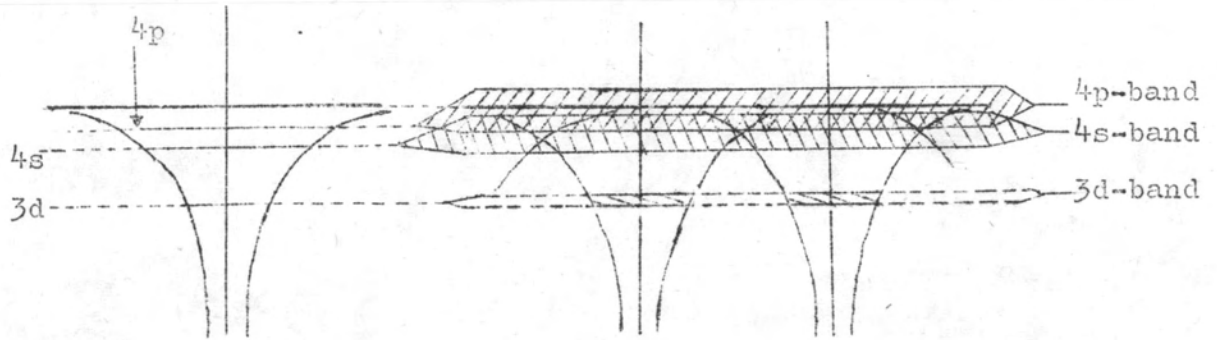
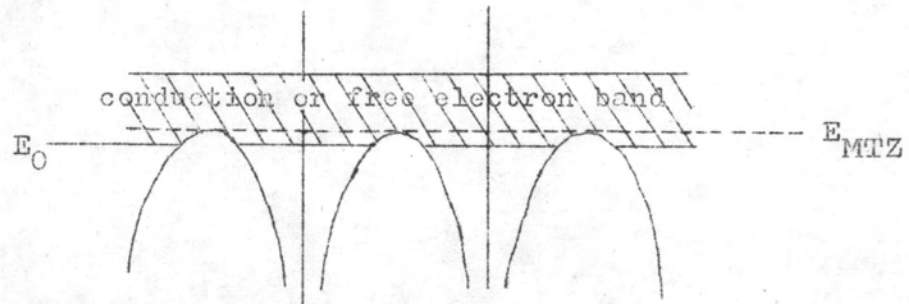
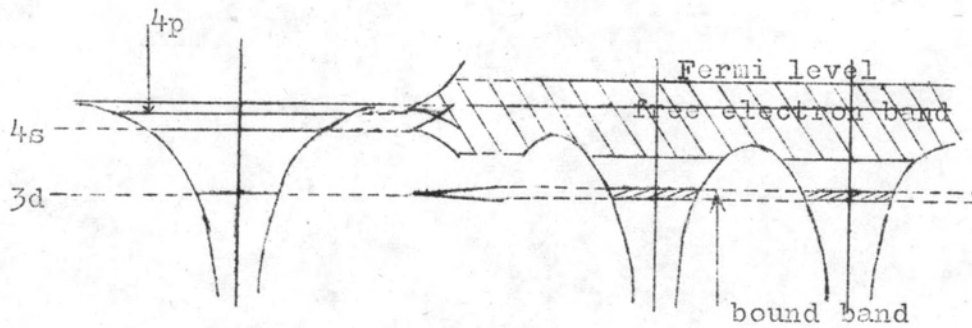


Fig. 5 Conventional LCAO description of the formation of metallic conduction bands.

(on the right). When a number of such atoms are brought together to form a solid, this not only allows the atomic orbitals on neighbouring sites to interact and form a band but also the overlap of potentials lowers the barrier between neighbouring cells to such an extent that some of the supposed "atomic levels" now lie above the muffin-tin zero and are no longer bound states of the muffin-tin wells. As the bands arising from distinct atomic levels begin to overlap one another in energy—such as 4s and 4p bands—they simply coalesce into a single nearly free electron distribution, referred as sp-bands. Atomic d-levels, however, form d-bands. These are shown in Fig. 6.



(a)



(b)

Fig. 6 (a) The bottom of free electron bands, E_0 , lie a little below the assumed muffin-tin zero, E_{MTZ} .

(b) Conventional LCAO description of the formation of metallic conduction bands in terms of the muffin-tin potentials.

1.b) d-bands and resonances

It is known for transition metals that 3d-atomic orbitals are fairly small compared with other (sp) valence states of comparable energy. The radial extension of 3d-states decreases exponentially at a shorter distance from the origin than that of 4s-states as shown in Fig. 7. As a result, the d-states are fairly localized; they are not strongly perturbed by the lattice potential and cannot overlap very strongly the atomic states of other nearby atoms. Hence the d-bands are narrow compared with the nearly free electron bands formed from atomic s- and p-states.

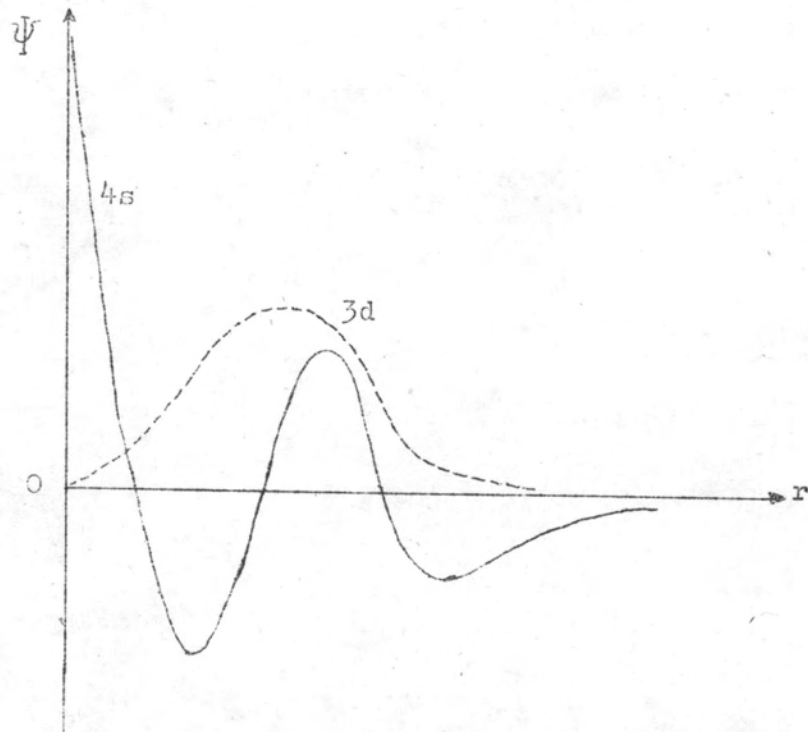


Fig. 7 Radial extension of a 4s- and a 3d-states for a transitional atom (schematic).



In 3d-transition metals, the atomic d-level lies above the flat portion of the muffin-tin potential. The centrifugal barrier $l(l+1)/r^2$ with $l=2$ is dominant over the atomic potential in a core for a d-electron, as schematically illustrated in Fig. 8. The bands are schematically illustrated on an E-k diagram in Fig. 9(b) which shows the bottom of the conduction band to coincide roughly with the energy corresponding to the flat portion of the muffin-tin potential. Electrons with considerably lower energy would no longer be free to spread out over the entire crystal. The different five bound states of d-electron are degenerate at the atomic d-level energy, E_d , which lies above the constant part of the muffin-tin potential in the case of the iron-series transition metals. In a solid, these d-levels are loosely bound and lie within the conduction band continuum, and, in the conventional language, hybridize with it. The d-band lies relatively close to the atomic zero above the muffin-tin constant energy. This information is borne out in the results of first-principles band calculations. This situation is interpreted in the following lines.

The atomic levels of angular momentum $l=2$ are not completely destroyed in solid but become virtual or resonance levels. The term $l(l+1)/r^2$, contained in the radial Schrödinger equation of $l=2$ (d-electron case) behaves like the potential of a centrifugal force repelling the electron from the region of the nucleus. In this bound state of $l=2$, the d-electron is confined in the annular space between the centrifugal barrier and the ordinary external Coulomb potential of the atom, i.e. the d-level has a strong tendency for

its wave function to concentrate within the atom. When atoms are brought together to form a solid, the repulsive potential acts as a barrier and inhibits the spread of d-levels over the crystal because the outer barrier is not completely lost but still interposes a hill through which the electron in the original atomic level must tunnel if it is to decay into a plane wave state of the same energy.

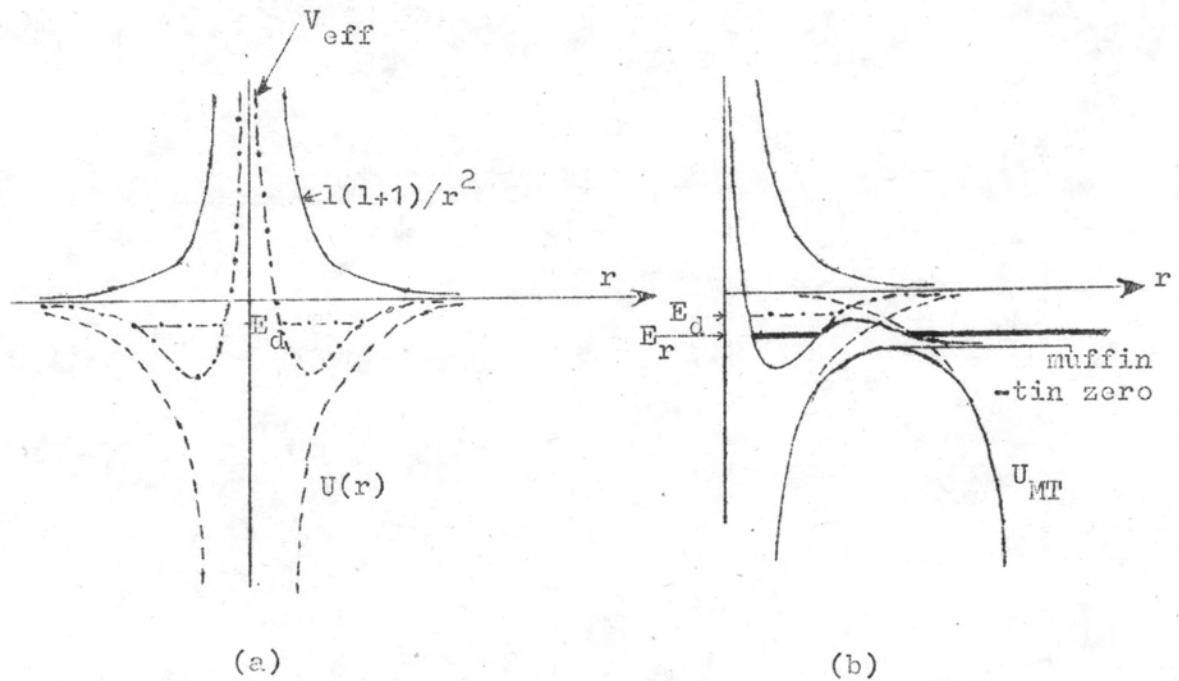


Fig. 8 (a) The addition of the centrifugal energy $l(l+1)/r^2$ to the atomic potential $U(r)$ gives rise to an effective potential V_{eff} with bound state at E_d ($l=2$ case).
 (b) The overlapping of atomic potentials to produce a muffin-tin potential U_{MT} turns the d-bound state, E_d , into a resonance at E_r , above the muffin-tin zero.

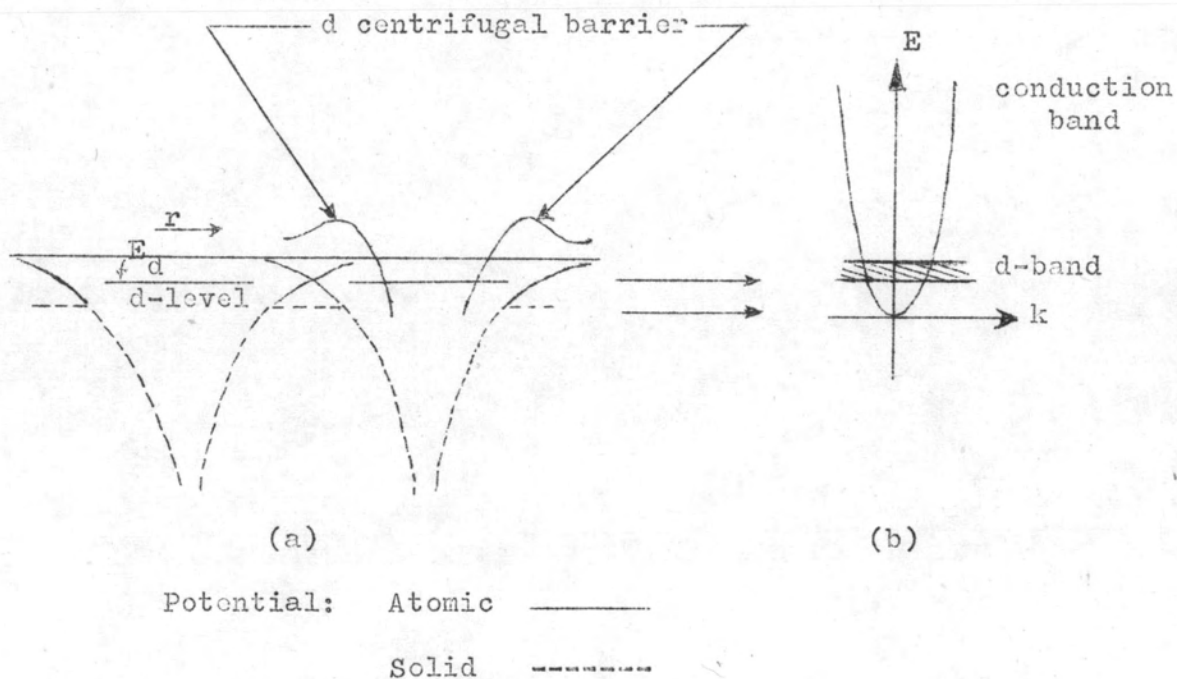


Fig. 9 (a) Showing the existence of the d centrifugal barrier and the crystal potential in the muffin-tin approximation (dashed lines) as well as the position of the atomic d-level in the iron-series transition metals relative to the flat portion of the muffin-tin.

(b) Showing the relative position of the conduction band and the d-band.

2. Heine's formulation

To solve the electronic band structure in the one-electron approximation

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

with a periodic crystal potential $V(\underline{r})$ in the so-called "muffin-tin" approximation, it is well-known that one may regard the atomic potential located at each lattice site as an elastic scatterer characterized by a given phase shift. Because of the constant potential in the region the incident and scattered particles can be represented as plane waves in the interstitial region, i.e. the space between the inscribed spheres centered on neighbouring sites. The band structure calculation can therefore be formulated as a scattering problem in a periodic array characterized by the KKR secular equation

$$\det \left| A_{lm;lm'} + \kappa \delta_{ll'} \delta_{mm'} \cot \eta_l \right| = 0 \quad \dots 2)$$

which involves only the structure constants $A_{lm;lm'}$ and the phase shifts η_l associated with each scatterer for energy $E = \kappa^2$. Explicit expressions for the preceding quantities have been given in eq. II.43) (here after this notation refers to the eq. 43) in chapter II). Ziman has transformed this KKR secular equation of real space representation into a form appropriate to the solution of the pseudopotential problem in plane wave representation. The result is written in the form

$$\det \left| \left\{ (\underline{K}_n + \underline{k})^2 - E \right\} \delta_{nn'} + \overline{\square}_{nn'}^{(Z)} \right| = 0. \quad \dots 3)$$

This equation is called the KKR-Z secular equation. It is similar to the NFE formula but we have to replace the pseudopotential matrix elements of the NFE case by the KKR-Z formula

$$\overline{\square}_{nn'}^{(Z)} = \frac{4\pi}{\mathcal{C}} \sum_l (2l+1) \tan \eta'_l \frac{j_l(k_n r_i) j_l(k_{n'} r_i) P_l(\cos \theta_{nn'})}{j_l^2(k r_i)} \dots 4)$$

The symbol k_n stands for $|\underline{K}_n + \underline{k}|$; $\underline{k}_n = \underline{K}_n + \underline{k}$. (\underline{K}_n are reciprocal lattice vectors and \underline{k} is the propagation vector.) κ^2 is the kinetic energy relative to the muffin-tin zero, r_i the radius of the inscribed sphere and \mathcal{C} the atomic volume. j_l and n_l are the usual spherical Bessel and Neumann functions. $P_l(\cos \theta_{nn'})$ is the Legendre polynomial and $\theta_{nn'}$ is the angle between \underline{k}_n and $\underline{k}_{n'}$. The modified phase shift η'_l is related to the true phase shift η_l of the l th partial wave through the formula

$$\cot \eta'_l(\kappa) = \cot \eta_l(\kappa) - n_l(\kappa r_i) / j_l(\kappa r_i). \quad \dots 5)$$

We have obtained eqs. 4) and 5) by putting the undefined variables r and r' as r_i . The KKR-Z equation is merely a reformulation of the KKR equation and it is still an exact formula which is also valid for any muffin-tin potential. The state of energy E in the KKR-Z representation is constructed as if it were a mixture of plane wave free electron states with pseudopotential matrix elements $\overline{\square}_{nn'}^{(Z)}$.

$\overline{\square}_{nn'}^{(Z)}$ depend on the scatterers only through a trigonometric function of the phase shifts η_l on the energy shells. A strong

potential producing a large phase shift can be replaced by a weaker pseudopotential, since the true phase shift η_1 and a smaller one differing from it by integral multiples of π produce the same $\square_{nn'}^{(Z)}$. How this is possible follows from the consideration of the scattering expressed in terms of phase shifts. Let us write the true phase shifts in the form

$$\eta_1 = p_1\pi + \delta_1 \quad \dots 6)$$

where p_1 are integers such that $|\delta_1| < \frac{\pi}{2}$. It is well-known in quantum theory that phase shift formulae for scattering involve $\exp(2i\eta_1)$, therefore integral multiples of π do not contribute to the formulae and the scattering can be determined from the reduced phase shifts δ_1 which is relatively small for bands of NFE behaviour, e.g. sp-bands formed from the atomic s- and p-states. In the case of transition metals, their band structures cannot be described purely in terms of the NFE model because of the d-bands. The KKR-Z secular equation 3) remains valid but $\square_{nn'}^{(Z)}$ is no longer a weak pseudopotential. The d-scattering becomes strong and highly energy dependent at the energy where the nearly free electron band crosses the d-bands. According to the KKR-Z formula, we now have to focus attention on this behaviour in terms of d-phase shift. To get at the phase shift behaviour in the region of the d-band, we consider a single transition metal atom placed in a free electron gas with the d-level, E_d , of the atom a little above the bottom of the plane wave band, as it is in solid. The d-state has a finite life time \hbar/W because an electron in it may escape into a plane wave of the same energy, exactly as in nuclear theory of an alpha particle tun-

nelling out of the nucleus. In the present case, the electron has to pass through the centrifugal barrier $l(l+1)/r^2$ with $l=2$ in the radial Schrödinger equation which is about 1 rydberg positive at the edge of the atom where the atomic potential has become zero. In this situation, the interaction between an incoming plane wave and the atomic d-state is the resonance interaction in the $l=2$ phase shift²³, i.e.

$$\tan \eta_2 = \frac{\frac{1}{2}W}{E_{d-res} - E} \quad \dots 7)$$

where the width of the resonance W is related to the life time \hbar/W of the virtual bound state or the resonance state by the uncertainty principle and E_{d-res} is the position of atomic d-resonance. In metal E_{d-res} is measured relative to the muffin-tin constant.

As a result of the so-called "cancellation theorem"^{1, 2, 3} of the pseudopotential theory, the pseudopotential matrix elements $\overline{V}_{nn'}(Z)$ for conduction bands arising from s- and p-atomic levels turn out to be small (i.e. the terms for $l=0, 1$). Hence we may write

$$\overline{V} = \overline{V}_{NFE} + \overline{V}_{d-res} \quad \dots 8)$$

where the second term arises from the behaviour 7) and gives all the features associated with the d-bands. In particular the width and shape of the d-band, as well as the hybridization, must all be related

²³ L. D. Landau and E. M. Lifshitz, Quantum Mechanics (Pergamon Press, Inc., London, 1958), 441-443.

to the single constant W in eq. 7) since E_{d-res} just specifies the position of d-band relative to the muffin-tin constant. The main consequence of the resonance point of view is that the d-d interaction in the band structure arises from the interference between resonances on neighbouring sites.

The set of eqs. 3), 4) and 5) forms the starting point of Heine's derivation of his model Hamiltonian. In his derivation, the 3d wave function is assumed to be that of an atomic 3d function inside the inscribed sphere in the atomic cell and it becomes a spherical Bessel function with asymptotic behaviour outside the sphere. In other words, we have assumed the 3d-wave functions to behave as the bound state atomic wave functions with exponentially decreasing tail inside whereas the wave functions associated with resonant states involve long oscillatory tails outside the muffin-tin sphere.

The parameter W is evaluated by making use of the integral formula for phase shift and by taking the narrow band approximation, i.e. three-center integrals are neglected. Introducing some further approximations, Heine obtained the $l=2$ contribution to the pseudo-potential as

$$-\sum_m \frac{\gamma_{nm}^* \gamma'_{nm}}{E_{d-res} - E} + V_{2,nn'} + (E - E_{d-res}) \sum_m b_{nm}^* b'_{nm} \quad \dots 9)$$

where $\delta_{nm} = \langle \varphi_m | V | \underline{k}_n \rangle, \quad \dots 10)$

$$b'_{nm} = \langle \varphi_n | \underline{k}_{n'} \rangle, \quad \dots 11)$$

$$V_{2,nn'} = \langle \underline{k}_{-n} | VP_2 | \underline{k}_{-n'} \rangle \dots 12)$$

m denotes the magnetic quantum number of d-wave functions and $\underline{k}_{-n} = \underline{K}_{-n} + \underline{k}$; \underline{K}_{-n} is the reciprocal lattice vector. $|\varphi_m\rangle$ is the ket of the complete d-orbital and V is the potential acting on $l=2$ waves. $|\underline{k}_{-n}\rangle$ is the plane wave normalized over the unit cell corresponding to $\exp[i(\underline{K}_{-n} + \underline{k}) \cdot \underline{r}]$ and P_2 is a projection operator to pick out the $l=2$ component. The first term of eq. 9) reflects the resonance scattering of the electrons from the d-levels. The second term is the $l=2$ contribution to the nn' Fourier components of the potential V . The last term is the usual orthogonality term of an orthogonalized plane wave secular equation²⁴. The latter two terms describe the scattering of plane waves explicitly orthogonalized to the d-functions by the crystal potential. The KKR-Z secular equation, still expressed entirely in a plane wave representation, can be written as

$$\det X = \det \left| C_{nn'} - \sum_m \frac{\gamma_{nm}^* \gamma_{nm}}{E_{d-res} - E} \right| = 0, \dots 13)$$

$$\text{with } C_{nn'} = (|\underline{K}_{-n} + \underline{k}|^2 - E)\delta_{nn'} + \sum_l V_{l,nn'} + (E - E_{d-res}) \sum_m b_{nm}^* b_{nm} \dots 14)$$

where $l=0, 1$ terms are expressed, for brevity, as Fourier components $V_{l,nn'}$ of the pseudopotential;

²⁴ J.M. Ziman, Principles of the theory of solids (Cambridge University Press, Cambridge, England, 1964).

$$V_{l,nn'} = \langle \underline{k}_{-n} | VP_l | \underline{k}_{-n'} \rangle, \quad \dots 15)$$

where P_l are operators projecting out l -components. The $l = 0, 1$ terms of eq. 14) are associated with the weak nonresonant part of the pseudopotential scattering.

In order to arrive at the model Hamiltonian, a matrix identity

$$\begin{bmatrix} C & \gamma^* \\ \tilde{\gamma} & D \end{bmatrix} \times \begin{bmatrix} I & 0 \\ -D^{-1}\tilde{\gamma} & I \end{bmatrix} = \begin{bmatrix} C - \gamma^* D^{-1}\tilde{\gamma} & \gamma^* \\ 0 & D \end{bmatrix} \quad \dots 16)$$

is introduced with $D^{-1} = (E_{d\text{-res}} - E)^{-1} \delta_{mm'}$ and $\det D = (E_{d\text{-res}} - E)^5$.

Then

$$\det Z = \det \begin{vmatrix} C_{nn'} & \gamma_{nm}^* \\ \tilde{\gamma}_{nm} & (E_{d\text{-res}} - E) \delta_{mm'} \end{vmatrix} = 0 \dots 17)$$

becomes

$$\det Z = \det \left[C - \gamma^* D^{-1} \tilde{\gamma} \right] \cdot \det D = 0, \quad \dots 18)$$

$$\det Z = \det X \cdot (E_{d\text{-res}} - E)^5 = 0. \quad \dots 19)$$

This result tells us that the secular equation of determinant Z is equivalent to that of determinant X since the factor $(E_{d\text{-res}} - E)^5$ is of no consequence.

In order to describe the band structures of transition metals up to and including the first band gap of the NFE part, we wish to have an effective Hamiltonian with a limited number of plane waves. Since we need only four plane waves in a faced-centered cubic (fcc)

structure we want to decouple them from the higher plane waves.

We write eq. 17) in the form

$$\det \begin{vmatrix} C_{hh'} & C_{hn'} & \delta_{hm'}^* \\ \tilde{C}_{nh'}^* & C_{nn'} & \delta_{nm'}^* \\ \tilde{\gamma}_{mh'} & \tilde{\gamma}_{mn'} & (E_{d-res} - E) \delta_{mm'} \end{vmatrix} = 0. \quad \dots 20)$$

The rows and columns of this determinant are labelled by the magnetic quantum numbers m corresponding to $l=2$ and by the reciprocal lattice vectors. The latter have been divided into two groups: \underline{K}_n are those few smallest reciprocal lattice vectors that must be retained in the interpolation scheme in order to obtain an adequate description of the conduction bands, and \underline{K}_h are the higher reciprocal lattice vectors. To eliminate the terms connecting $C_{hh'}$ with the rest, we use the transformation

$$\begin{bmatrix} A & B \\ \tilde{B}^* & F \end{bmatrix} \times \begin{bmatrix} I & -A^{-1}B \\ -F^{-1}\tilde{B}^* & I \end{bmatrix} = \begin{bmatrix} A-BF^{-1}\tilde{B}^* & 0 \\ 0 & F-\tilde{B}^*A^{-1}B \end{bmatrix} \dots 21)$$

where

$$A = C_{hh'} , \quad \dots 22)$$

$$B = \begin{bmatrix} C_{hn'} & \delta_{hm'}^* \end{bmatrix} , \quad \dots 23)$$

$$F = \begin{bmatrix} C_{nn'} & \delta_{nm'}^* \\ \tilde{\gamma}_{mn'} & (E_{d-res} - E) \delta_{mm'} \end{bmatrix} . \quad \dots 24)$$

It follows from eqs. 20) and 21) that

$$\det \begin{vmatrix} A - BF^{-1}\tilde{B}^* & 0 \\ 0 & F - \tilde{B}^*A^{-1}B \end{vmatrix} = 0. \quad \dots 25)$$

Now the determinant of eq. 20) is proportional to the product of the two subdeterminants of eq. 25) and the roots of the former considered as a secular equation are to be found in the latter pair. We find that our desired secular equation is in the lower right position of the determinant of eq. 25) and this leads to a secular determinant of the form

$$\det \begin{vmatrix} C'_{nn'} & \gamma'^*_{nm} \\ \tilde{\gamma}'_{mn'} & D'_{mm'} \end{vmatrix} = 0. \quad \dots 26)$$

Here $C'_{nn'}$ has the same form as $C_{nn'}$ of eq. 14) except that the pseudo-potentials are renormalized by higher order contributions from the higher plane waves;

$$C'_{nn'} = C_{nn'} - (\tilde{V}^*)_{nh}(C^{-1})_{hh'}V_{hn'} \quad \dots 27)$$

$\tilde{\gamma}'$ is the "renormalized" interaction matrix with elements

$$(\tilde{\gamma}'^*)_{nm'} = \gamma^*_{nm'} - (\tilde{V}^*)_{nh}(C^{-1})_{hh'}\gamma^*_{hm'} \quad \dots 28)$$

Finally the d-band part of eq. 21) is

$$D'_{mm'} = D_{mm'} - \tilde{\gamma}_{mh}(C^{-1})_{hh'}(\tilde{\gamma}'^*)_{hm'} \quad \dots 29)$$

of which the lowest order term is given by

$$D'_{mm'} \sim D_{mm'} - \sum_h \frac{\tilde{\gamma}_{mh} \gamma^*_{hm'}}{|k+K_h|^2 - E},$$

or

$$D'_{mm'} \sim (E_{d-res} - E) \delta_{mm'} - \sum_h \frac{\tilde{\gamma}_{mh} \gamma_{hm}^*}{|\underline{k} + \underline{K}_h|^2 - E} \dots 30)$$

The d-d part or $D'_{mm'}$ may be shown to correspond approximately to a tight-binding form involving only two-center integrals for both positive and negative energies. Heine's proof of positive energies depends on the recognition that a great deal of destructive interference exists among the long tails of φ_m which originate from every lattice site. For fcc lattices, the determinant of eq. 26) is 9×9 and contains four plane waves \underline{K}_n and five d-functions m . The $C'_{nn'}$ and γ'_{nm} , respectively, describe the conduction bands and the hybridization between these and the d-bands. It should be noted that $D'_{mm'}$ depend on the crystal potential through the matrix elements γ_{hm} having the same form as those determining the hybridization.

Eq. 26) is closely related to the equation which forms the departure point for the interpolation scheme given in chapter I. The physical interpretation of the model Hamiltonian analytically derived by Heine, i.e. eq.26), is as follows. The transformation which reduces the KKR-Z secular equation of the form 13) into eq. 26) 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 characterizes tight-binding theory must arise from such indirect interactions according to the present description. This description leads to the ambiguity in Heine's theory because the plane waves \underline{K}_n which are retained to describe the conduction bands hybridize with the d-bands

and in this way also produce an additional interaction among d-functions centered on different sites. That is, to obtain the tight-binding form of the d-bands, we have to transform away all plane waves K_n and K_h . However, this difficulty has been circumvented in subsequent works. For example, Hubbard's scheme is achieved by introducing a cut off parameter at the early stage in his theory to distinguish K_n and K_h explicitly.¹⁰ Its effect is to alter the proportion of the interaction between d-states occurring directly via the two-center integrals appearing in D'_{mm} and indirectly through the hybridization matrix elements.

The physical contents of the formalism which has been sketched may be presented pictorially as shown in Fig. 9 and Fig. 10. The Fig. 9(a) has already been discussed. As a result of the resonant scattering by the periodic array, a broadened d-band, shown in Fig. 9(b), is obtained which is degenerate with and therefore hybridizes with the conduction band. The details of the hybridization are illustrated in Fig. 10, which shows the band structure of an fcc metal like Cu or Ni along the [100] direction. The d- and conduction bands shown in Figs. 10(a) and 10(b) would be obtained respectively from a solution of the D'_{mm} and C'_{nn} blocks, of eq. 26). Because of the presence of terms involving b_{nm} in eq. 14) which guarantee the orthogonalization of the conduction states to the d-band wave functions, the effective pseudopotential coefficients, and hence the gaps in the iron-series conduction bands, can be considerably larger than those of unhybridized conduction bands. Finally the χ'_{nm} blocks produce the hybridization between the pure d- and conduction bands having the

same symmetry (labelled by Λ_1) as is illustrated in Fig. 10(c).

The effect of hybridization is to split the unhybridized bands apart where they would otherwise cross. In general directions in the Brillouin zone the situation is similar, except for the differences in the degeneracy of d-bands and the effect of hybridization on the d-bands.

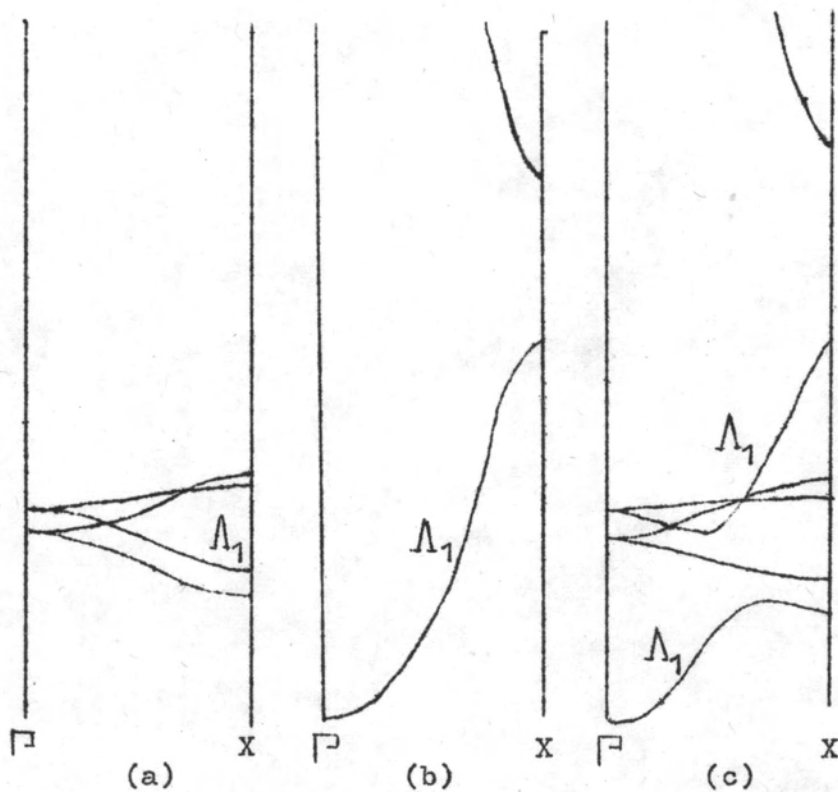


Fig. 10 Energy bands of an fcc transition metal along $[100]$ direction, before and after hybridization.

- (a) d bands before hybridization
- (b) conduction bands before hybridization
- (c) hybridized d and conduction bands Λ_1 .

5. Hubbard's scheme without cut off parameter

This section is devoted to a detailed derivation of Hubbard's first-principles theory for the approximate calculation of transition-metal band-structures.

The present theory is obtained by suitable modification and refinement of Heine's work.⁹ Hubbard's theory may be considered more successful than others as it does not require any adjustable parameters, thus permitting more flexible applications. The starting point of Hubbard's argument is Ziman's formulation of the KKR method of Korringa, Kohn and Rostoker. Ziman's determinantal equation is approximately transformed to a low-order secular equation whose roots give approximately the energy levels.

The basis of the theory is Ziman's transformed KKR equation which is generalized into

$$\det \left| (k_n^2 - E) \delta_{nn'} + \Gamma_{nn'}(Z) \right| = 0 \quad \dots 31)$$

where

$$\begin{aligned} \Gamma_{nn'}(Z) &= \Gamma_{(k_n, k_{n'})}, \\ &= -\frac{4\pi}{\kappa r_1} \sum_l (2l+1) \tan \eta_l' \frac{j_l(k_n r_1) j_l(k_{n'} r_1) P_l(\cos \theta_{nn'})}{j_l^2(\kappa r_1)} \end{aligned} \quad \dots 32)$$

and

$$\cot \eta_l' = \cot \eta_l - n_l(\kappa r_1) / j_l(\kappa r_1). \quad \dots 33)$$

The notations used here are the same as those of the preceding section except that r_1 is used instead of r_i . Here we have denoted

$\underline{k}_n + \underline{k}$ by \underline{k}_n ; \underline{k}_n being a vector of the reciprocal lattice. In these formulae, r_l are chosen arbitrarily on the interval $(0, r_i)$ where r_i is the radius of the inscribed sphere of the atomic polyhedron. Actually, eq. 31) is a generalization of Ziman's equation since the r_l 's for different l in eq. 32) have not been required to be equal. One may verify the correctness of these formulae by suitably generalizing Ziman's discussion given in chapter II. $\theta_{nn'}$ is the angle between \underline{k}_n and $\underline{k}_{n'}$. According to the present description, the matrix elements of the pseudopotential, $V_{nn'}^{(Z)}$, depend mainly on phase shifts of the atomic potentials, the wave vector \underline{k} and the energy of the Bloch state being considered. The contributions from various l are defined at the different r_l 's.

Eq. 32) may be rearranged to give

$$V_{nn'}^{(Z)} = \frac{4\pi}{\tau} \sum_l (2l+1) \left[- \frac{\tan \eta_l'}{\kappa j_l^2(\kappa r_l)} \right] j_l(\kappa_n r_l) j_l(\kappa_{n'} r_l) P_l(\cos \theta_{nn'}). \quad \dots 34)$$

Using eq. 33), we have

$$\begin{aligned} \tan \eta_l' &= \frac{1}{\cot \eta_l - n_l(\kappa r_l)/j_l(\kappa r_l)}, \\ &= \frac{j_l(\kappa r_l) \cdot \tan \eta_l(\kappa)}{j_l(\kappa r_l) - \tan \eta_l(\kappa) n_l(\kappa r_l)}. \quad \dots 35) \end{aligned}$$

The multiplication of eq. 35) by $\left[- \frac{1}{\kappa j_l^2(\kappa r_l)} \right]$ gives

$$- \frac{\tan \eta_l'}{\kappa j_l^2(\kappa r_l)} = - \frac{\tan \eta_l(\kappa)}{\kappa j_l(\kappa r_l) [j_l(\kappa r_l) - \tan \eta_l(\kappa) n_l(\kappa r_l)]}$$

Defining

$$\gamma_1 = - \frac{\tan \eta_1(k)}{kr_1^2 j_1(kr_1) [j_1(kr_1) - \tan \eta_1(k) n_1(kr_1)]}, \dots 36)$$

we have

$$- \frac{\tan \eta_1}{kj_1^2(kr_1)} = r_1^2 \gamma_1, \dots 37)$$

and instead of eq. 34) we obtain

$$\Gamma_{nn'} = \frac{4\pi}{\mathcal{V}} \sum_{\mathbf{l}} (2l+1) r_1^2 \gamma_1 j_l(k_n r_1) j_l(k_{n'} r_1) P_l(\cos \theta_{nn'}), \dots 38)$$

which is a generalization of Slater's formula²⁵. The secular equation 31) with the form of Γ given by eq. 38) is now the condition under which the simultaneous equations

$$(k_n^2 - E) B_n + \sum_{n'} \Gamma_{nn'} B_{n'} = 0 \dots 39)$$

have nontrivial solutions. Lloyd²⁶ showed that the B_n 's are coefficients of a plane wave expansion of a pseudo-wavefunction which coincides with the true wavefunction in the region between the boundaries of the atomic polyhedron (of volume \mathcal{V}) and its inscribed sphere:

$$\Psi_{ps}(\underline{r}) = (1/\mathcal{V})^{1/2} \sum_{\mathbf{n}} B_{\mathbf{n}} \exp(i\mathbf{k}_{\mathbf{n}} \cdot \underline{r}) = \Psi_{\underline{k}}(\underline{r}), \dots 40)$$

²⁵ J.C. Slater, "Green's Function Method in the Energy Band Problem," Physical Review B, 145, 599-602(1966).

²⁶ P. Lloyd, "Pseudo-potential Models in the Theory of Band Structure," Proceeding of Physical Society of London, 86, 825-832(1965).

the first equality holding throughout the atomic polyhedron but the second equality only in the region outside the inscribed sphere.

To verify that eq. 39) is really the generalization of Slater's equation, one substitutes $1/\kappa r_1^2$ by the Wronskian $[j_1(\kappa r_1), n_1(\kappa r_1)]$ in eq. 36), so that

$$\begin{aligned} \gamma_1 &= - \frac{\tan \eta_1(\kappa) [j_1(\kappa r_1), n_1(\kappa r_1)]}{j_1(\kappa r_1) [j_1(\kappa r_1) - \tan \eta_1(\kappa) n_1(\kappa r_1)]}, \\ &= \frac{j_1(\kappa r_1) \{j_1'(\kappa r_1) - \tan \eta_1 n_1'(\kappa r_1)\} - j_1'(\kappa r_1) \{j_1(\kappa r_1) - \tan \eta_1 n_1(\kappa r_1)\}}{j_1(\kappa r_1) [j_1(\kappa r_1) - \tan \eta_1(\kappa) n_1(\kappa r_1)]}, \\ &= L_1 - \frac{j_1'(\kappa r_1)}{j_1(\kappa r_1)}, \quad \dots 41) \end{aligned}$$

and putting $r_1 = r_i$ we have

$$\gamma_1 = L_1 - \frac{j_1'(\kappa r_i)}{j_1(\kappa r_i)} \quad \dots 42)$$

where L_1 is the logarithmic derivative of the solution $R_1(r)$ of the radial Schrödinger equation for the energy E at $r=r_i$.

Suppose first that one is dealing with a simple metal rather than a transition metal. According to the KKR scheme of band structure calculation applied to a muffin-tin form of potential, the potential figures in the calculation only in determining the phase shifts which are energy dependent. For this case the pseudopotential is weak. This implies that the tangents of the phase shifts η_1 remain small throughout the energy range of interest for band structure calculations. It follows from eqs. 36) and 38) that γ_1 and $\left[\frac{\gamma}{nn'} \right]$ will

be small except when $j_1(kr_1)$ or $j_1(kr_1) - \tan \eta_1 n_1(kr_1)$ is near zero for some l . However, by suitably adjusting the r_1 within the prescribed range $(0, r_i)$ one can prevent the latter situation from occurring. For example one may, following Pendry and Capart²⁷, take r_1 to be given by the zero of $n_1(kr_1)$ provided there is a zero in $(0, r_i)$ and otherwise take $r_1 = r_i$; such a choice will ensure that the two factors in the denominator of eq. 36) remain of order unity and that the smallness of $\tan \eta_1$ will imply the smallness of δ_1 . In fact Pendry's prescription for r_1 was used throughout the calculations by Hubbard; only for $l=0$, r_1 is found to differ from r_i in the range of energies considered in his calculations.

Suppose now that one is dealing instead with a transition metal for which $\tan \eta_2$ passes through a narrow resonance at low energy. In this case no amount of adjustment of r_2 will prevent the appearance of a corresponding narrow infinity in δ_2 at energy near the resonance in $\tan \eta_2$. Thus one may conclude that, provided the r_1 are chosen according to Pendry's prescription, the δ_1 will in general be small except near the narrow resonance in $\tan \eta_2$; δ_2 will have a narrow resonance in this neighbourhood. On the basis of this argument we may write

$$\delta_1 = \delta_1' - \int_{1\lambda} \frac{\Gamma}{E_0 - E} \cdot \dots \quad (43)$$

Here there is assumed to be only one resonance occurring for the $l = \lambda$ wave ($\lambda = 2$ for a transition metal) at an energy $E = E_0$; the sign has been chosen to make $\Gamma > 0$ where Γ denotes the width of the reso-

²⁷ J.B. Pendry and G. Capart, "The Choice of Muffin-tin Pseudopotential," Journal of Physics C (Solid state physics), [2], 2, 841-851 (1969).

nance of δ_1 . δ_1' is the residue of δ_1 after the resonance of $l = \lambda$ wave has been subtracted. All δ_1' are now small and smoothly varying functions of E .

Substituting eq. 43) into eq. 38) and eq. 38) into eq. 39), one obtains

$$(k_n^2 - E)B_n + \sum_{n'} \frac{4\pi}{\tau} \sum_l (2l+1)r_l^2 \left[\delta_1' - \delta_{1\lambda} \frac{\Gamma}{E_0 - E} \right] j_l(k_n r_l) j_l(k_{n'} r_l) \\ \cdot P_l(\cos \theta_{nn'}) B_{n'} = 0,$$

or

$$(k_n^2 - E)B_n + \frac{4\pi}{\tau} \sum_{l, n'} (2l+1)r_l^2 \delta_1' j_l(k_n r_l) j_l(k_{n'} r_l) P_l(\cos \theta_{nn'}) B_{n'} \\ - \frac{4\pi}{\tau} \sum_{n'} (2\lambda+1)r_\lambda^2 \frac{\Gamma}{E_0 - E} j_\lambda(k_n r_\lambda) j_\lambda(k_{n'} r_\lambda) P_\lambda(\cos \theta_{nn'}) B_{n'} \\ = 0. \quad \dots 44)$$

Using the addition theorem

$$P_\lambda(\cos \theta_{nn'}) = \frac{4\pi}{2\lambda+1} \sum_{m=-\lambda}^{\lambda} Y_{\lambda m}(\hat{k}_n) Y_{\lambda m}^*(\hat{k}_{n'}), \quad \dots 45)$$

one gets instead of eq. 44),

$$(k_n^2 - E)B_n + \frac{4\pi}{\tau} \sum_{l, n'} (2l+1)r_l^2 \delta_1' j_l(k_n r_l) j_l(k_{n'} r_l) P_l(\cos \theta_{nn'}) B_{n'} \\ - \frac{(4\pi r_\lambda)^2}{\tau} \frac{\Gamma}{E_0 - E} \sum_m j_\lambda(k_n r_\lambda) Y_{\lambda m}(\hat{k}_n) \sum_{n'} j_\lambda(k_{n'} r_\lambda) Y_{\lambda m}^*(\hat{k}_{n'}) B_{n'} \\ = 0. \quad \dots 46)$$

Defining

$$a_m = \frac{4\pi r_\lambda}{E_0 - E} \left\{ \frac{\Gamma}{\tau} \right\}^{1/2} \sum_n j_\lambda(k_n r_\lambda) Y_{\lambda m}^*(\hat{k}_n) B_n, \quad \dots 47)$$

eq. 46) becomes

$$(k_n^2 - E)B_n + \frac{4\pi}{c} \sum_{l, n'} (2l+1)r_l^2 \gamma_l' j_l(k_n r_l) j_l(k_n r_l) P_l(\cos \theta_{nn'}) B_{n'} - 4\pi r_\lambda \left\{ \frac{\rho}{c} \right\}^{\frac{1}{2}} \sum_m j_\lambda(k_n r_\lambda) Y_{\lambda m}(\hat{k}_n) a_m = 0,$$

or

$$(k_n^2 - E)B_n + \sum_{n'} V_{nn'} B_{n'} + \sum_m h_{nm} a_m = 0, \quad \dots 48)$$

where

$$V_{nn'} = \frac{4\pi}{c} \sum_l (2l+1)r_l^2 \gamma_l' j_l(k_n r_l) j_l(k_n r_l) P_l(\cos \theta_{nn'}), \quad \dots 49)$$

$$h_{nm} = -4\pi r_\lambda \left\{ \frac{\rho}{c} \right\}^{\frac{1}{2}} j_\lambda(k_n r_\lambda) Y_{\lambda m}(\hat{k}_n). \quad \dots 50)$$

Eq. 47) may be rewritten as

$$(E_0 - E)a_m - 4\pi r_\lambda \left\{ \frac{\rho}{c} \right\}^{\frac{1}{2}} \sum_n j_\lambda(k_n r_\lambda) Y_{\lambda m}^*(\hat{k}_n) B_n = 0,$$

$$(E_0 - E)a_m + \sum_n h_{nm}^* B_n = 0. \quad \dots 51)$$

The equations 48) and 51) are equivalent to eq. 39), so that Ziman's determinantal equation, with the form of eq. 43) for γ_l , must be equivalent to

$$\det \begin{vmatrix} K + V - EI & h \\ h^* & (E_0 - E)I \end{vmatrix} = 0. \quad \dots 52)$$

Here V is a matrix with elements $V_{nn'}$ given by eq. 49),

h is a matrix with elements h_{nm} given by eq. 50),

h^* is the Hermitian conjugate of h ,

I are unit matrices of the appropriate orders,

and K is a diagonal matrix with elements $k_n^2 \delta_{nn'}$.

The bottom -right-hand submatrix is of order $(2\lambda+1)$. We may state in another way that eq. 39) is equivalent to the matrix equation

$$\begin{bmatrix} K + V - EI & h \\ h^* & (E_0 - E)I \end{bmatrix} \begin{bmatrix} B \\ a \end{bmatrix} = 0 \quad \dots 53)$$

where B is the column matrix containing the nonresonant part of the wave function and a is the column matrix describing the resonant behaviour of the pseudo-wave-function $\Psi_{ps}(\underline{r})$.

Next, the determinantal equation 52) is reduced to a low order equation by the procedure used by Heine. First, the various vectors \underline{k}_n are divided into two sets: a "preferred" set P containing only the few \underline{k}_n for which \underline{k}_n^2 lies in or near the energy range of interest, and a "remainder" set R containing all \underline{k}_n not in P.

The preferred set P is chosen in the following way. Suppose one is interested in calculating the energy levels lying in some prescribed energy range for some prescribed range of the wave vector \underline{k} , then the preferred set P is taken to consist of all those $\underline{k}_n = \underline{k} + \underline{K}_n$ which are such that for some values of \underline{k} within the prescribed range of \underline{k} the value of \underline{k}_n^2 lies in or near the energy range of interest (values within 1 rydberg of the energy range of interest were found to be suitable in practice). This choice of the set P ensures that, if \underline{k}_n belongs to the remainder set R, then $E - \underline{k}_n^2$ never vanishes or becomes small for any choice of \underline{k} or E of interest.

Corresponding to this partitioning of the \underline{k}_n into two sets P and R, the determinant may also be partitioned into the form

$$\det \begin{vmatrix} K_R + V_{RR} - EI & V_{RP} & h_R \\ V_{PR} & K_P + V_{PP} - EI & h_P \\ h_R^* & h_P^* & (E_0 - E)I \end{vmatrix} = 0 \dots 54)$$

Now the choice of the sets P and R ensures that no diagonal element of K_P can be degenerate or nearly degenerate with any diagonal element of K_R . It follows that the elements of V_{RP} can affect the roots of this equation at most in second order. However, the matrix elements of V_{RP} are small because the γ'_l are small (cf. eq. 49), and so one may introduce into eq. 54) the approximation of putting $V_{RP} = V_{PR} = 0$. When this has been done, we have instead of eq. 54)

$$\det \begin{vmatrix} K_R + V_{RR} - EI & 0 & h_R \\ 0 & K_P + V_{PP} - EI & h_P \\ h_P^* & h_R^* & (E_0 - E)I \end{vmatrix} = 0 \dots 55)$$

We next apply the technique used by Heine in order to decouple the preferred set of plane waves from the remainder set by using the transformation

$$\begin{bmatrix} A & B \\ \tilde{B}^* & C \end{bmatrix} X \begin{bmatrix} I & -A^{-1}B \\ -C^{-1}\tilde{B}^* & I \end{bmatrix} = \begin{bmatrix} A - BC^{-1}\tilde{B}^* & 0 \\ 0 & C - \tilde{B}^* A^{-1}B \end{bmatrix} \dots 56)$$

Putting

$$A = [K_R + V_{RR} - EI], \dots 57)$$

$$B = [0 \quad h_R], \dots 58)$$

$$C = \begin{bmatrix} K_P + V_{PP} - EI & h_P \\ h_P^* & (E_0 - E)I \end{bmatrix}, \dots 59)$$

then the determinant of eq. 55) is proportional to the product of two subdeterminants corresponding to

$$\left[A - BC^{-1}\tilde{B}^* \right] \left[C - \tilde{B}^* A^{-1} B \right] = 0. \quad \dots 60)$$

The roots of eq. 55) are now determined from the secular equations of the subdeterminants of eq. 60), i.e.

$$\det \left| A - BC^{-1}\tilde{B}^* \right| = 0, \quad \dots 61)$$

$$\det \left| C - \tilde{B}^* A^{-1} B \right| = 0. \quad \dots 62)$$

We find that our desired secular equation is of the form 62), i.e.

$$\det \left| \begin{array}{cc} K_P + V_{PP} - EI & h_P \\ h_P^* & (E_0 - E)I \end{array} \right| - \begin{array}{c} \left[0 \\ h_R^* \right] \\ \left[K_R + V_{RR} - EI \right]^{-1} \left[0 \quad h_R \right] \end{array} = 0,$$

$$\det \left| \begin{array}{cc} K_P + V_{PP} - EI & h_P \\ h_P^* & (E_0 - E)I - h_R^* \left[K_R + V_{RR} - EI \right]^{-1} h_R \end{array} \right| = 0 \dots 63)$$

Since matrix elements V_{RR} are small compared with $\frac{k_{-n}^{2(R)}}{-n} - E$ (the subscript (R) denotes that k_{-n} belong to the set R), we drop the V_{RR} in eq. 63) and write

$$\det \left| \begin{array}{cc} K_P + V_{PP} - EI & h_P \\ h_P^* & A - EI \end{array} \right| = 0 \quad \dots 64)$$

where the matrix A is defined by

$$A \equiv E_0 I - h_R^* \left[K_R - EI \right]^{-1} h_R. \quad \dots 65)$$

In this way eq. 52) is reduced to a low order determinantal equation 64). The band structure can now be determined by finding the energies $E(\underline{k})$ which are the eigen values of the determinantal equation 64). Eq. 64) corresponds to the matrix equation of the form

$$\begin{bmatrix} K_P + V_{PP} - EI & h_P \\ h_P^* & A - EI \end{bmatrix} \begin{bmatrix} B_P \\ a \end{bmatrix} = 0 \quad \dots \quad 66)$$

where the eigen vector contains the preferred and resonant parts of the pseudo-wave function. The order of the determinant is $n_P + 5$ for a d-resonance case where n_P is the number of preferred vectors (typically n_P is of the order 4-7).

For convenience, we drop the subscript P in eq. 64) and rewrite

$$\det \begin{vmatrix} K + V - EI & h \\ h^* & A - EI \end{vmatrix} = 0 \quad \dots \quad 67)$$

where the matrix elements of V and h are still given by eqs. 49) and 50) and the $(2\lambda+1) \times (2\lambda+1)$ matrix A is given by

$$A_{mm'} = E_0 \delta_{mm'} - (4\pi r_\lambda)^2 \frac{\Omega}{c} \sum_n^{(R)} \frac{j_\lambda^2(k_n r_\lambda) Y_{\lambda m}^*(\hat{k}_n) Y_{\lambda m}(\hat{k}_n)}{k_n^2 - E} \dots \quad 68)$$

The sum $\sum_n^{(R)}$ is over all vectors of the set R.

So far our problem has been reduced to that of solving the low-order determinantal equation 64) or 67) with the aid of the approximations that have been introduced. Once the phase shifts are given the computational problem is reduced to that of summing the series in eq. 68), and solving the determinantal equation 67).



Regarding the computation of the series in eq. 68), it may be noted that it is not very rapidly convergent. However, this difficulty may be overcome by approximating the sum over all \underline{k}_n for which k_n is greater than some large enough value k_0 by the corresponding integral. To be more precise, one writes

$$\sum_n^{(R)} \frac{j_\lambda^2(k_n r_\lambda)}{k_n^2 - E} Y_{\lambda m}^*(\hat{k}_n) Y_{\lambda m}(\hat{k}_n) \simeq \sum_n^{(S)} \frac{j_\lambda^2(k_n r_\lambda)}{k_n^2 - E} Y_{\lambda m}^*(\hat{k}_n) Y_{\lambda m}(\hat{k}_n) + \int_{k > k_0} \frac{j_\lambda^2(|\underline{k} + \underline{k}'| r_\lambda)}{(\underline{k} + \underline{k}')^2 - E} Y_{\lambda m}^*(\widehat{(\underline{k} + \underline{k}')}) Y_{\lambda m}(\widehat{(\underline{k} + \underline{k}')}) \frac{d\underline{k}'}{\tau_k} \dots 69)$$

where the sum $\sum_n^{(S)}$ is over all those \underline{k}_n of the first few shells of the reciprocal lattice vectors (typically of the order 50-100 vectors in practice) excluding those of the preferred set P, $\tau_k = (2\pi)^3 / \mathcal{C}$ is the volume of the unit cell in reciprocal lattice space, and k_0 is chosen so that

$$\frac{4\pi}{3} \frac{k_0^3}{\tau_k} = n \dots 70)$$

where n is the total number of \underline{k}_n in the preferred set plus those included in the $\sum_n^{(S)}$ sum. If the n and k_0 used in practice were sufficiently large (to the required accuracy) then one could neglect \underline{k} compared with \underline{k}' and E compared with k'^2 in the evaluation of the integral in eq. 68). We have

$$I \equiv \int_{k' > k_0} \frac{j_\lambda^2(|\underline{k} + \underline{k}'| r_\lambda)}{(\underline{k} + \underline{k}')^2 - E} Y_{\lambda m}^*(\widehat{(\underline{k} + \underline{k}')}) Y_{\lambda m}(\widehat{(\underline{k} + \underline{k}')}) \frac{d\underline{k}'}{\tau_k},$$

$$I \sim \int_{k' > k_0} \frac{j_\lambda^2(kr_\lambda)}{k'^2} Y_{\lambda m}^*(k) Y_{\lambda m}(k') \frac{dk'}{C_k} \dots 71)$$

For the $\lambda = 2$ case, we make an additional approximation by using the asymptotic form of $j_2(kr_\lambda)$;

$$j_2(kr_\lambda) \underset{kr_\lambda \rightarrow \infty}{\sim} \frac{1}{kr_\lambda} \sin(kr_\lambda - \frac{2\pi}{2}) = -\frac{\sin(kr_\lambda)}{kr_\lambda} \dots 72)$$

then the integral in eq. 71) is now rewritten as

$$I \sim \int_{k' > k_0} \frac{\sin^2(kr_\lambda)}{k'^4 r_\lambda^2} Y_{\lambda m}^*(k) Y_{\lambda m}(k') \frac{dk'}{C_k},$$

$$I = \int_{k' > k_0} \frac{1 - \cos(2kr_\lambda)}{2k'^4 r_\lambda^2} Y_{\lambda m}^*(k) Y_{\lambda m}(k') \frac{k'^2 \sin \theta dk' d\theta d\varphi}{C_k} \dots 73)$$

Using the orthonormality relation

$$\int_0^{2\pi} \int_0^\pi Y_{\lambda m}^*(k) Y_{\lambda m}(k') \sin \theta d\theta d\varphi = \delta_{mm'} \dots 74)$$

eq. 73) becomes

$$I = \frac{\delta_{mm'}}{r_\lambda C_k} \left[\int_{k' > k_0} \frac{1}{2k'^2 r_\lambda} dk' - \int_{k' > k_0} \frac{\cos(2kr_\lambda)}{2k'^2 r_\lambda} dk' \right] \dots 75)$$

The first term on the right of eq. 75) yields

$$\int_{k' > k_0} \frac{1}{2k'^2 r_\lambda} dk' = \frac{1}{2r_\lambda} \left\{ -\frac{1}{k'} \right\} \Big|_{k'=k_0}^{\infty},$$

$$= \frac{1}{2k_0 r_\lambda}, \quad \dots 76)$$

and the term

$$\int_{k' > k_0} \frac{\cos(2k'r_\lambda)}{2k'^2 r_\lambda} dk' = \int_{2k'_\lambda > 2k_0 r_\lambda} \frac{\cos(2k'_\lambda)}{(2k'_\lambda)^2} d(2k'_\lambda),$$

$$= \int_{t > 2k_0 r_\lambda} \frac{\cos t}{t^2} dt,$$

$$= - \int_{t > 2k_0 r_\lambda} \cos t d\left\{\frac{1}{t}\right\},$$

$$= - \left[\frac{\cos t}{t} \Big|_{t=2k_0 r_\lambda}^{\infty} + \int_{t > 2k_0 r_\lambda} \frac{\sin t}{t} dt \right],$$

$$= \frac{\cos(2k_0 r_\lambda)}{2k_0 r_\lambda} - \int_0^{\infty} \frac{\sin t}{t} dt + \int_0^{2k_0 r_\lambda} \frac{\sin t}{t} dt,$$

$$= \frac{\cos(2k_0 r_\lambda)}{2k_0 r_\lambda} - \frac{\pi}{2} + \int_0^{2k_0 r_\lambda} \frac{\sin t}{t} dt \dots 77)$$

Substituting eqs. 76) and 77) into eq. 75), we obtain

$$\begin{aligned}
 I &= \frac{\delta_{mm'}}{r_\lambda \tau_k} \left[\frac{1}{2k_0 r_\lambda} - \frac{\cos(2k_0 r_\lambda)}{2k_0 r_\lambda} + \frac{\pi}{2} - \int_0^{2k_0 r_\lambda} \frac{\sin t}{t} dt \right], \\
 &= \frac{\delta_{mm'}}{r_\lambda \tau_k} \left[\frac{1 - \cos X}{X} + \frac{\pi}{2} - \text{Si}(X) \right]_{X=2k_0 r_\lambda} \quad \dots 78)
 \end{aligned}$$

where $\text{Si}(X)$ is the sine integral

$$\int_0^X \frac{\sin t}{t} dt.$$

22

In calculations worked out by Hubbard, this approximation was used for the integral and it was found that the sum $\sum_n^{(s)}$ could be quite rapidly evaluated including 50-100 terms.

To solve the determinantal equation 67) efficiently is very difficult since multiple roots are likely to occur. A possible method for solving it is that used in the usual augmented-plane-wave (APW) or Korringa-Kohn-Rostoker (KKR) methods, i.e. to evaluate the determinant at many energies belonging to a sufficiently small interval in E and the determination for the roots is usually achieved by interpolation.