s-d Interaction in Transition Metals*

VOLKER HEINE†

Department of Physics and Institute for the Study of Metals, The University of Chicago, Chicago, Illinois

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It has been shown recently that the calculated electronic band structure of transition metals may be represented quite precisely by a model Hamiltonian with a nearly-free electron *sp* band crossing and hybridizing with a tight-binding *d* band. The form of this model Hamiltonian is now exhibited as a transformation of the fundamental Korringa-Kohn-Rostoker formulation of the energy-band problem. The hydridization appears as a resonance between a localized *d* state and the plane-wave band. In addition to throwing light on some details of the model Hamiltonian, the derivation serves to express some of its constituents in terms of simple atomic quantities. In particular, the structure and width of the *d* band and the hybridization are all related to one *intra*-atomic matrix element. The *d* band appears as an interference between resonances, its shape determined by purely geometrical structure constants and its width by the width of the resonance. These relations are demonstrated quantitatively for the band structure of copper.

I. INTRODUCTION AND OUTLINE

THERE are three ingredients to the present work. Saffren,[1] Ehrenreich and co-workers,[2] and Mueller[3] have shown that the electronic band structure of copper, up to somewhat above the Fermi level, may be fitted very well by a model Hamiltonian of four orthogonalized plane waves hybridizing with five tight-binding 3*d* functions. Secondly, Anderson and McMillen,[4] among others,[5,6] have emphasized that the hybridization springs not so much from a true *s-d* interaction mediated by a nonspherical symmetric potential, as from a resonance interaction with the *l*=2 component of the plane waves. Indeed, they found this gives rise to some of the structure of the *d*-band in a model of "liquid iron." Finally, Ziman[6] has shown formally from the Korringa-Kohn-Rostoker (KKR) method[7,8] that one must get the kind of band structure one finds,[9,10] if one postulates a 3*d*-resonant state in a plane-wave band.

The first purpose of this paper is to carry Ziman's analysis[6] further in Sec. II and derive in detail the model Hamiltonian in Sec. III. At the energy where the nearly-free-electron (NFE) band crosses the *d* band, the interaction between them is a resonance interaction with a phase shift

$$\eta_2 = \tan^{-1}(\tfrac{1}{2}W/(E_d - E)). \tag{1}$$

At energies high above E_d, the dynamical effect of the 3*d* states on the plane waves (PW) is to make them into orthogonalized plane waves (OPW). We formulate therefore in Sec. II the PW-*d* interaction in a complete, consistent, phase-shift formalism embracing both the hybridization and orthogonalizing effects. We find in Sec. III that they give terms in the model Hamiltonian precisely as postulated by Mueller.[3] It becomes apparent from the derivation why the hybridization interaction cuts off for *k* somewhat beyond the radius of the first Brillouin zone,[3] contrary to what one would expect simply by calculating a PW hybridization integral. This also serves to explain partly the approximate sum rules of Phillips.[11] At the same time we find an important extra potential term not included explicitly by Mueller,[3] the omission explaining why his orthogonality coefficients differ radically from what one would calculate from an atomic *d* orbital in the usual OPW manner. The omission also explains why he finds the main $L_{2'}L_1$ band gap in the NFE band given largely by *d* effects, whereas simple estimates from atomic energies would suggest that it is largely due to *s-p* splittings. We should emphasize that we are only interested in the band structure of one electron, or rather one Landau quasiparticle, moving in the periodic effective potential. We also restrict ourselves to the nonmagnetic state, although extension to a ferromagnetic one is formally straightforward. We do not concern ourselves with the question (considered by Hubbard[12] and others) of when some magnetic state is energetically favorable. Incidentally, we assume the model Hamiltonian, with trivial changes for the body-centered cubic (bcc) structure, applies to all transition metals. Besides Cu,[1–3,13] it has been applied successfully so far to Ag,[13] Au,[13] Ni,[2,14] and bcc Fe,[15] and the band structures of other transition metals as far as they are known are qualitatively similar.

[1] M. Saffren, in *The Fermi Surface*, edited by W. A. Harrison and M. B. Webb (John Wiley & Sons, Inc., New York, 1960), p. 341.
[2] L. Hodges and H. Ehrenreich, Phys. Letters **16**, 203 (1965); L. Hodges, H. Ehrenreich, and N. D. Lang, Phys. Rev. **152**, 505 (1966).
[3] F. M. Mueller, Phys. Rev. **153**, xxx (1967).
[4] P. W. Anderson and W. McMillen (unpublished).
[5] See, for example, F. M. Mueller and J. C. Phillips (unpublished).
[6] J. M. Ziman, Proc. Phys. Soc. (London) **86**, 337 (1965).
[7] J. Korringa, Physics **13**, 392 (1947).
[8] W. Kohn and N. Rostoker, Phys. Rev. **94**, 1111 (1954). Equations in this paper will be identified by the abbreviation KR.
[9] B. Segall, Phys. Rev. **125**, 109 (1962).
[10] G. A. Burdick, Phys. Rev. **129**, 138 (1963).

[11] J. C. Phillips, preceding paper, Phys. Rev. **153**, 669 (1967).
[12] See, for example, J. Hubbard, Proc. Phys. Soc. (London) **84**, 455 (1964), and references therein.
[13] R. Jacobs (unpublished).
[14] E. Zornberg (unpublished).
[15] G. Weisz (unpublished).

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 different atoms. Let us consider one copper atom placed in a free-electron gas. If we integrate outwards from the origin at an energy E_d, the wave function inside the sphere of radius R inscribed in an atomic cell is approximately an atomic $3d$ function;

$$\Phi_m(r<R)=\phi_m\equiv\phi(r)Y_{lm}(\theta,\phi). \qquad (2a)$$

Here ϕ is a radial d function normalized according to $\int\phi^2 r^2 dr=1$, ϕ_m is the complete d orbital, and Y_{lm} is the usual spherical harmonic. The function is contained by the "centrifugal barrier" $l(l+1)/r^2$ of the radial wave equation, and once outside it, Φ_m becomes a spherical Bessel function behaving asymptotically as[16]

$$\Phi_m(r>R)\sim(W/2K)^{1/2}r^{-1}\sin(Kr-\tfrac{1}{2}l\pi+\eta)Y_{lm}. \qquad (2b)$$

Here K^2 is E_d, the energy of the resonance above the bottom of the free-electron band. Equation (2b) is proportional to $W^{1/2}$ because W in (1) is essentially the probability[16] of the state ϕ_m "escaping from the barrier" or "decaying into the plane-wave states."

The d-d part of the model Hamiltonain derived in Sec. III is almost identical with the $l=2$ submatrix of the KKR secular equation, and in the Appendix we rederive it in the approximation of a narrow band by a "tight-binding" calculation with the orbitals Φ of (2). That this is possible is not immediately obvious because the tail (2b) stretches to infinity and Φ is not normalizable. However, it turns out that the tight-binding Bloch functions formed from Φ are normalizable because there is so much destructive interference among the tails from all the atomic sites. The outer part of ϕ merges into the first hump of the phase-shifted function, and if one pictures the overlap with the first shell of nearest neighbors, it will not differ much from that of the more usual atomic orbitals. However, there are some qualitative differences from the normal tight-binding theory, because the energy E_d lies above the bottom of the plane-wave band, so that Φ does not decrease exponentially at large distances. We find that in the limit of a narrow band ($W\to 0$) the three-center integrals disappear and *all* two-center integrals become proportional to W. The latter can be seen as follows. A two-center integral is

$$\langle\Phi(\text{site0})\,|\,V(\text{site0})\,|\,\text{tail from site }\mathbf{s}\rangle. \qquad (3)$$

One factor of $W^{1/2}$ comes from the amplitude of the tail. The remaining integral is, apart from irrelevant factors, the matrix element

$$\gamma(\mathbf{k}_0, m_k=0)=\langle\phi_0|\,V\,|\mathbf{k}_0\rangle, \qquad (4)$$

where $|\mathbf{k}_0\rangle$ is a plane wave of energy E_d with $\mathbf{k}_0$ parallel

to the axis of quantization of the $m=0$ function ϕ_0. Now (4) is just the transition matrix element governing the probability W of a particle escaping from the well. Thus (4) gives a further factor of $W^{1/2}$ and (3) is proportional to W. We note that the contribution of distant neighbors is of the same order in W as near ones, though presumably much reduced by interference. The remainder of (3) is a purely geometrical quantity connected with the expansion of the tail centered at $\mathbf{s}$ in terms of spherical Bessel functions and spherical harmonics centered at the site zero. Dividing through by W, we obtain a 5×5 secular equation for the d band

$$\det\|(\text{const})B_{mm'}-[(E-E_d)/\tfrac{1}{2}W]\delta_{mm'}\|=0, \qquad (5)$$

where the B's are determined by the geometrical factors. They turn out to be in fact just the structure constants of the KKR method,[8] and we are back to the same secular equation as found for the d-d part of the effective Hamiltonian in Sec. III. The analysis in the Appendix establishes therefore that the d band can indeed be interpreted in terms of the overlap of resonance orbitals $\Phi(2)$ centered at each atom, exactly as in the tight-binding method except that the term "tight" binding is here a misnomer since the orbitals are unbound.

Finally, in Sec. IV we illustrate the usefulness of (5) for numerical and analytical work. We show that our arguments can be substantiated quantitatively for the band structure of copper as calculated by Segall.[9] The KKR structure can be determined from tables[17,18] as a function of $\mathbf{k}$ and E. If we set E in the B's equal to the mean position E_d of the band, then the *shape* of the d band is determined purely by the structure constants, and its *scale* by the hybridizing interaction W. Moreover, it is the same W that gives the hybridization splitting which can be seen[9] in $E(\mathbf{k})$ between the d band and the plane-wave band where they would otherwise cross. $W^{1/2}$ can be evaluated from (4), the vital part of which is what we term the reduced matrix element

$$M=\int V\phi r^4 dr. \qquad (6)$$

We have estimated M by graphical integration from the Chodorow potential[19] which is very close to the $l=2$ potential used by Segall,[9] using for ϕ a Hartree-Fock orbital. The only quantity taken from Segall's band-structure results is the mean energy E_d of the d band above the bottom of the plane-wave band. With simply a slide rule we can then calculate the hybridization splitting between the d band and the plane-wave band, and with the tabulated KKR structure con-

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[16] L. D. Landau and E. M. Lifshitz, *Quantum Mechanics* (Pergamon Press, Inc., London, 1958), pp. 441–3.

[17] B. Segall and F. S. Ham (unpublished). A copy of this report may be obtained as described in Ref. 18.
[18] F. S. Ham, Phys. Rev. **128**, 82 (1962).
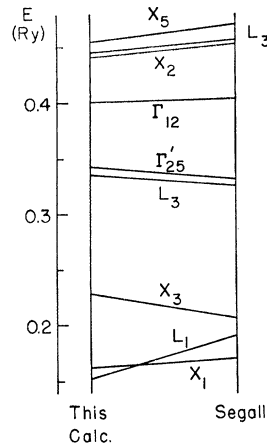[19] Taken from the table in Ref. 10.

FIG. 1. Symmetry levels in the d band of Cu calculated by the method of Sec. IV and compared with Segall's results (Ref. 9).

stants,[17,20] the levels of the d band. The main energies in the d band at symmetry points are compared with Segall's[9] in Fig. 1. The over-all agreement is excellent within the 10% accuracy of some of our estimates. Our levels L_1 and X_1 lie lower than Segall's, as they should, because we have neglected the big L_1L_2' and X_1X_4' band gaps as explained in Sec. IV. Incidentally, we note in connection with our discussion of Eq. (5), that although Segall's d bands are considerably wider than those of Burdick, the *ratios* of the overlap integrals are nearly the same, resulting in bands of very nearly *the same shape*.

It is interesting that the width of the d band in (5) is determined through W by the *intra*-atomic matrix element (4), (6). No *inter*-atomic overlap integrals of the *normal* kind enter our formulation of the d band. The ratio between the different overlap integrals, if one expresses the d band in tight-binding terms,[2,3,21] is contained implicitly in the structure constants B. Conventional atomic overlap integrals are difficult to calculate reliably in solids, and still more so their *change with interatomic distance*. However, in our theory we might expect the intra-atomic reduced matrix element (6) to remain constant under small changes of structure or volume of the metal. Our method should therefore allow calculation of the changes in band structure with strain or more complex distortions, relating to measurements of the piezoreflectance of transition metals and the whole formulation of the electron-phonon interaction. This hope is borne out by the first such calculations,[13] which will be presented elsewhere, namely, a simple volume change in Cu and Ag where the predictions of the theory are checked against detailed band-structure calculations. Since we have shown that it is fundamentally valid to describe the d band in tight-binding terms, a simple volume change should establish the variation of the overlap

integrals with distance, and this in turn determine the change of band structure under a shear strain without the necessity of ever having to recalculate the KKR constants for the sheared structure.

II. THE SECULAR EQUATION

For monatomic crystals Ziman[6] has derived the form (in units $\hbar = 2m = 1$)

$$\det\|(|\mathbf{k}-\mathbf{g}|^2 - E)\delta_{\mathbf{g}\mathbf{g}'} + \Gamma_{\mathbf{g}\mathbf{g}'}\| = 0 \qquad (7)$$

for the secular equation for the band structure, where

$$\Gamma_{\mathbf{g}\mathbf{g}'} \equiv \Gamma(\mathbf{k}-\mathbf{g}, \mathbf{k}-\mathbf{g}')$$

$$= \sum_l \left[-\frac{(4\pi)^2 N}{K} \tan\eta_l' \right]\left[\frac{j_l(|\mathbf{k}-\mathbf{g}|R)j_l(|\mathbf{k}-\mathbf{g}'|R)}{j_l(KR)j_l(KR)} \right]$$

$$\times [\sum_m Y_{lm}*(\mathbf{k}-\mathbf{g})Y_{lm}(\mathbf{k}-\mathbf{g}')], \qquad (8)$$

$$\cot\eta_l' = \cot\eta_l - [n_l(KR)/j_l(KR)]. \qquad (9)$$

Here η_l is the phase shift, K^2 is the energy E, N^{-1} is the volume of the unit cells, R is the radius of the inscribed sphere, and the other symbols have their usual meaning as defined by Ziman.[6] In his formalism, the spherical harmonics Y_{lm} were chosen in such linear combinations that they were all real, but that restriction is not necessary in what follows. The argument $\mathbf{k}-\mathbf{g}$ of Y_{lm} denotes the angular direction of the vector $\mathbf{k}-\mathbf{g}$. As regards the $l=0$ and 1 terms in (8), the phase shifts will be small (modulo π) because of the cancellation theorem,[22–24] and Γ corresponds to a weak pseudopotential as discussed already by Ziman.[6] He has also pointed out[6] that an $l=2$ phase shift of the form (1) will give something like a resonant, hybridizing interaction between the NFE and d bands.

We now consider the $l=2$ phase shift in greater detail. We first note that if η_2 is given by (1), then

$$\cot\eta_2' = (\tfrac{1}{2}W)^{-1}(E_d - E) - (n_2/j_2)_{KR}$$

$$= (\tfrac{1}{2}W)^{-1}(E_d' - E), \qquad (10)$$

where E_d' is a shifted-resonance energy

$$E_d' = E_d - \tfrac{1}{2}Wn_2(KR)/j_2(KR). \qquad (11)$$

Thus η_2' has the same structure (1) as η_2, and we shall henceforth drop the prime from E_d' for the sake of simplicity.

The parameter W can be evaluated by substituting (2), (3) into the integral formula for the phase shift.[25]

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[20] I am indebted to Roy Jacobs for letting me use his table of the C's which are the Clebsch-Gordan coefficients relevant to the particular definition of spherical harmonics used in Ref. 17.

[21] J. C. Slater and G. F. Koster, Phys. Rev. **94**, 1498 (1954).

[22] J. C. Phillips and L. Kleinman, Phys. Rev. **116**, 287 (1959).
[23] M. H. Cohen and V. Heine, Phys. Rev. **122**, 1821 (1961).
[24] B. J. Austin, V. Heine, and L. J. Sham, Phys. Rev. **127**, 276 (1962).
[25] A. Messiah, *Quantum Mechanics* (North-Holland Publishing Company, Amsterdam, 1961), p. 405. Note that the particular form of this reference requires ϕ of (2) to be multiplied by $(2K/W)^{1/2}$ for appropriate normalization.

At resonance $\eta_2'=\frac{1}{2}\pi$ and we obtain

$$(\tfrac{1}{2}W)^{1/2}=-K^{1/2}\int_0^\infty j_2(Kr)V\phi r^2 dr, \qquad (12)$$

where V is the potential acting on the $l=2$ wave. In the case of the $3d$ transition series, this is the full potential: for the $4d$ and $5d$ series it is a pseudopotential with $3d$ and $3d$, $4d$ cancellation, respectively.[23-24] Thus the first bracket in (8) becomes

$$-(4\pi)^2NK^{-1}\tan\eta_2'$$

$$=-\frac{\left[4\pi N^{1/2}\int_0^\infty j_2(Kr)V\phi r^2 dr\right]^2}{E_d-E}. \qquad (13)$$

We turn now to the opposite limit $E\gg E_d$. With the usual OPW construction,[26] we write

$$\psi(r)=j_2(Kr)-\beta\phi(r), \qquad (14)$$

$$\beta=\int_0^\infty j_2(Kr)\phi r^2 dr, \qquad (15)$$

and again substitute in the integral formula for the phase shift,[25] obtaining

$$\sin\eta_2'=-K\int_0^\infty j_2(Kr)Vj_2(Kr)r^2 dr$$

$$+K\beta\int_0^\infty j_2(Kr)V\phi r^2 dr. \qquad (16)$$

Here we have written η_2' rather than η_2 because the difference has already been absorbed into (13). In order to simplify the last term of (16), we write V as $-T+T+V$, where T is the kinetic-energy operator. The $-T$ operates forward on $j_2(Kr)$ giving a factor $K^2=E$ (since j_2 is just part of a plane wave), and the remaining Hamiltonian $H=T+V$ operates on ϕ, giving a factor E_d. Thus the last term of (16) becomes

$$-(E-E_d)\beta K\int_0^\infty j_2(Kr)\phi r^2 dr. \qquad (17)$$

Actually, ϕ is not strictly an eigenstate of H and we should include the asymptotic tail (2b) which makes a small contribution to the integral in (17). It can be evaluated with the Wronskian theorem,[27] and vanishes in the limit of a narrow resonance, so that we drop it. Since (16) applies at an energy where the scattering has become small, we ignore the difference between

sine and tan, and we write

$$-(4\pi)^2NK^{-1}\tan\eta_2'$$

$$=(4\pi)^2N\int_0^\infty [j_2(Kr)]^2Vr^2 dr+(E-E_d)$$

$$\times\left[4\pi N^{1/2}\int_0^\infty j_2(Kr)\phi r^2 dr\right]^2. \qquad (18)$$

Having obtained the two formulas (13), (18) in different energy regions, we now add them to give the variation of $\tan\eta_2'$ over the whole range. This procedure is justified by the fact that one obtains the first term of (18) together with (13) in a more careful treatment[28] of the resonance. Furthermore, in order for $\tan\eta_2'$ to have the correct K^{2l+1} analytic variation[29] near $K=0$, we need to interpret K in (11) as $E^{1/2}$, i.e., varying with energy, and not as its value E_d^2 at the resonance. This appeal to analytic properties is not just an empty gesture, since in some calculations[13] the d band straddles the zero of energy which in the derivation of (8) is the muffin tin constant.

The remaining two factors of (8) may now be grafted onto (13) and (18). The $j_2(Kr)$ in (13), (18) may to a very good approximation be replaced by $(Kr)^2$ over the range of integration which really extends only to R. The same applies to the j_2's in the middle factor of (8), and its effect is therefore simply to replace the two $j_2(Kr)$ in (13), (18) by $j_2(|\mathbf{k}-\mathbf{g}|r)$ and $j_2(|\mathbf{k}-\mathbf{g}'|r)$. As usual,

$$4\pi N^{1/2}i^2\sum_m j_2(kr)Y_{2m}(\mathbf{r})Y_{2m}^*(\mathbf{k}) \qquad (19)$$

is the $l=2$ component of the plane wave $|\mathbf{k}\rangle$ normalized over the unit cell. The last factor of (8) can therefore be incorporated in the integrals to express them in terms of plane-wave matrix elements. We have from (8), (13), (18), and (19) that the $l=2$ contribution to $\Gamma_{gg'}$ is

$$\frac{-\sum_m\gamma_{gm}^*\gamma_{g'm}}{E_d-E}+V_{2,gg'}+(E-E_d)\sum_m b_{gm}^*b_{g'm}, \qquad (20)$$

where

$$\gamma_{g'm}=\langle\phi_m|V|\mathbf{k}-\mathbf{g}'\rangle, \qquad (21)$$

$$b_{g'm}=\langle\phi_m|\mathbf{k}-\mathbf{g}'\rangle, \qquad (22)$$

$$V_{2,gg'}=\langle\mathbf{k}-\mathbf{g}|VP_2|\mathbf{k}-\mathbf{g}'\rangle, \qquad (23)$$

and P_2 is a projection operator to pick out the $l=2$ component. The last term of (20) is the usual orthogonality term of an OPW secular equation,[26] and the middle term the $l=2$ contribution to the $\mathbf{gg}'$ Fourier component of the potential. The secular equation (7),

[26] J. M. Ziman, *Principles of the Theory of Solids* (Cambridge University Press, Cambridge, England, 1964).
[27] Reference 25, p. 99.

[28] W. Brenig and R. Haag, in *Quantum Scattering Theory*, edited by M. Ross (Indiana University Press, Bloomington, Indiana, 1963), p. 64.
[29] Reference 25, p. 392.

still expressed entirely in a plane-wave representation, can therefore be written

$$\det X \equiv \det \left| \left| M_{gg'} - \frac{\sum_m \gamma_{gm}{}^* \gamma_{g'm}}{E_d - E} \right| \right| = 0, \qquad (24)$$

$$M_{gg'} = (|\mathbf{k} - \mathbf{g}|^2 - E)\delta_{gg'} + \sum_l V_{l,gg'}$$
$$+ (E - E_d) \sum_m b_{gm}{}^* b_{g'm}, \qquad (25)$$

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

III. THE MODEL HAMILTONIAN

In order to arrive at the model Hamiltonian, two transformations of (24) are necessary. Consider

$$\det Z \equiv \det \left| \left| \begin{matrix} M_{gg'} & \gamma_{gm}{}^* \\ \tilde{\gamma}_{g'm} & (E_d - E)\delta_{mm'} \end{matrix} \right| \right| = 0. \qquad (26)$$

Abbreviating the matrix $(E_d - E)\delta_{mm'}$ as C, we have the identity

$$\left| \begin{matrix} M & \gamma^* \\ \tilde{\gamma} & C \end{matrix} \right| \times \left| \begin{matrix} I & 0 \\ -C^{-1}\tilde{\gamma} & I \end{matrix} \right| = \left| \begin{matrix} M - \gamma^* C^{-1}\tilde{\gamma} & \gamma^* \\ 0 & C \end{matrix} \right|. \qquad (27)$$

Now C^{-1} is $(E_d - E)^{-1}\delta_{mm'}$ and $\det C = (E_d - E)^5$, whence (27) becomes

$$\det Z = (E_d - E)^5 \det X, \qquad (28)$$

which proves the equivalence of the secular Eqs. (26) and (24), the factor $(E_d - E)^5$ being 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. As usual in a face-centered cubic (fcc) structure we need four[3] (which we denote by **G**), and we want to decouple them from the higher plane waves (HPW, denoted by **h**). The principle is exactly the same as with nontransition metals.[30,31] We write (26) in the form

$$\left| \left| \begin{matrix} M_{hh'} & M_{hG'} & (\gamma^*)_{hm'} \\ (\tilde{M}^*)_{Gh'} & M_{GG'} & (\gamma^*)_{Gm'} \\ \tilde{\gamma}_{mh'} & \tilde{\gamma}_{mG'} & (E_d - E)\delta_{mm'} \end{matrix} \right| \right| \qquad (29)$$

and eliminate the terms connecting $M_{hh'}$ with the rest, using the transformation

$$\left| \begin{matrix} A & B \\ \tilde{B}^* & C \end{matrix} \right| \times \left| \begin{matrix} I & -A^{-1}B \\ -C^{-1}\tilde{B}^* & I \end{matrix} \right|$$
$$= \left| \begin{matrix} A - BC^{-1}\tilde{B}^* & 0 \\ 0 & C - \tilde{B}^* A^{-1}B \end{matrix} \right|. \qquad (30)$$

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[30] N. W. Ashcroft, Phil. Mag. **8**, 2055 (1963).
[31] P. W. Anderson, *Concepts in Solids* (W. A. Benjamin, Inc., New York, 1963), p. 37.

Here the first determinant on the left is proportional to the product of the two subdeterminants on the right, and the roots of the former considered as a secular equation are to be found in the latter pair. We take for B the matrix

$$[M_{hG'}(\gamma^*)_{hm'}], \qquad (31)$$

and find in the lower right position our desired secular equation

$$\det \left| \left| \begin{matrix} (M')_{GG'} & (\gamma^*)_{Gm'} \\ (\tilde{\gamma}')_{mG'} & D_{mm'} \end{matrix} \right| \right| = 0. \qquad (32)$$

Here γ' is the "renormalized" interaction matrix

$$(\gamma^*)_{Gm} - (\tilde{V}^*)_{Gh}(M^{-1})_{hh'}(\gamma^*)_{h'm}. \qquad (33)$$

Similarly, M' has the same form as M (25) except that the pseudopotentials are renormalized by higher order contributions

$$- (\tilde{V}^*)_{Gh}(M^{-1})_{hh'}V_{h'G'} \qquad (34)$$

from the HPW's. Finally, the d-band part of (41) is

$$D_{mm'} = (E_d - E)\delta_{mm'} - \tilde{\gamma}_{mh}(M^{-1})_{hh'}(\gamma^*)_{h'm}, \qquad (35)$$

of which the lowest order term is

$$(E_d - E)\delta_{mm'} - \sum_h \frac{\gamma_{mh}\gamma_{hm'}{}^*}{|\mathbf{k} - \mathbf{h}|^2 - E}. \qquad (36)$$

We multiply this by $-2K/W$, substitute in (21), and undo backwards the steps (19), (10), and (12) to obtain

$$-(2K/W)D_{mm'} = \sum_h \frac{F_{mh}F_{m'h}{}^*}{|\mathbf{k} - \mathbf{h}|^2 - E} - \delta_{mm'}K \cot\eta_2', \qquad (37)$$

$$F_{mh} = 4\pi N^{1/2} \frac{j_2(|\mathbf{k} - \mathbf{h}|R)}{j_2(KR)} Y_{2m}(\mathbf{k} - \mathbf{h}).$$

Equations (32) to (37) define our model Hamiltonian. We note the reduction to a 9×9 secular equation is in principle an exact procedure,[30,31] at the cost of the resultant matrix elements becoming energy-dependent. One hopes this is not large if the choice of separation has been judicious, and much of it can in any case be absorbed into the k dependence of the matrix elements by putting $E \approx k^2$ in the NFE band. The nearly-free-electron part M' and hybridization matrix elements have the form (25) and (21), except that the numerical magnitudes are altered by the higher order corrections. M' contains $l = 0, 1, 2$ pseudopotential matrix elements apart from the explicit display of the repulsive terms for $l = 2$ in OPW form. This is precisely the form used by Mueller,[3] while Ehrenreich and co-workers[2] absorb the OPW terms into the pseudopotential matrix elements.

In (29) the d band has zero width, and it is interesting that the hybridization γ_{hm} with higher plane waves provides the width and structure of the d band in (35) and (36). This presumably reflects the need for

short-wavelength components to correct the wave functions in the region of overlap. The hybridization remaining in the model Hamiltonian is therefore only a *residual* interaction, the long-wavelength part. This explains why Mueller's[3] hybridization matrix elements differ radically from what one would naively expect from (21). We estimate from (21), in the manner of Sec. IV,

$$\gamma_{km} = 24 j_2(0.6k) Y_{2m}(\mathbf{k}) \mathrm{Ry} , \tag{38a}$$

whereas Mueller gives[3]

$$\gamma'_{km} = 0.59 j_2(4.3k) Y_{2m}(\mathbf{k}) \mathrm{Ry} . \tag{38b}$$

Expansion of the Bessel functions shows that the two agree approximately at low k, but Mueller's cuts off much more rapidly at k around the radius of the Brillouin zone because this part of the bare hybridization has been transformed away into the structure of the d band.

The mathematical transformation between (29) and (32) gives some formal justification for the approximate partial effective-mass sum rules noted by Phillips.[11] Let us consider (29) truncated at some large finite number $h+4$ plane waves. An effective-mass sum rule is simply a statement of the invariance of the term in k^2 in the trace of the Hamiltonian, and the $(m^*)^{-1}$ sum over all bands for (29) must be $h+4$, the d bands contributing zero because of zero width. In the form (30) the upper left matrix would describe the h upper bands, which by the usual cancelation theorem[22-24] behave as nearly-free electrons and hence have an $(m^*)^{-1}$ sum close to h. This leaves the remaining lower $4+5$ bands of our model Hamiltonian with an $(m^*)^{-1}$ sum close to 4. The sum rules exhibited by Phillips[11] are special cases of this at symmetry points.

In order to investigate the nature of the d band, let us arbitrarily extend the summation in (37) over all $\mathbf{g}$'s, i.e., include the four $\mathbf{G}$'s, and consider the resulting 5×5 secular equation in isolation. Comparison with Ref. 8 shows it is precisely the $l=2$ part of the KKR secular equation:

$$\det \| B_{2m,2m'} - \delta_{mm'} K \cot\eta_2 \| = 0 . \tag{39}$$

Including the four $\mathbf{G}$'s in the summation affects all the d levels at a general point $\mathbf{k}$, but only one state along ΓX and ΓL with Δ_1 and Λ_1 symmetry, respectively, these are the hybridizing states. For the remaining states the $\gamma'_{k-G,m}$ are zero for the lowest two $\mathbf{G}$'s by symmetry and small for the other two $\mathbf{G}$'s because the effective hybridization matrix elements cut off at large $|\mathbf{k}-\mathbf{G}|$, let us call these the pure d states. We can say precisely how much hybridization the 5×5 equation contains: The energy denominators in (37) or comparison with the full KKR equation with $\eta_0 = \eta_1 = 0$ shows (39) contains hybridization with a pure free-electron band, and K must now be measured with respect to the bottom of that band. By substituting (1)

into (39) we may write it as

$$\det \left\| \left(\frac{2\pi W}{Ka} \right) \left(\frac{a B_{2m2m'}}{4\pi} \right) - (E - E_d) \delta_{mm'} \right\| = 0 . \tag{40}$$

Beeby and Edwards[32] have shown that the KKR equation may be transformed to tight-binding form in the case of negative energies where the atomic orbitals decrease exponentially with distance. In the Appendix we give a proof for positive energies which shows that the d-d part (40) of the model Hamiltonian can be interpreted as due simply to the overlapping of resonant orbitals Φ_m, Eq. (2), on all the atomic sites $\mathbf{s}$. We construct, exactly as in the tight-binding method, the Bloch function

$$\psi_{km}(\mathbf{r}) = N^{1/2} \sum_{\mathbf{s}} \exp(i\mathbf{k} \cdot \mathbf{s}) \Phi_m(\mathbf{r}; \mathbf{s}) , \tag{41}$$

and prove that the Hamiltonian matrix in such a representation gives exactly the secular equation (40) in the limit $W \to 0$ of a narrow band. One point of interest emerges. The structure constants B in (40) depend on energy as well as $\mathbf{k}$. If in them we set E to the mean value E_d, we obtain a band whose width is proportional to W and whose shape is determined by the B's. The results in Fig. 1 were calculated in that way, and the excellent agreement with Segall[9] for the structure of the band as regards the pure d states suggests that it is a good approximation. Now in the analysis of the Appendix we find that this approximation is equivalent to taking two center integrals only, the three center integrals contributing an infinitesimal fraction of the bandwidth as $W \to 0$. In Mueller's scheme,[3] the shape of the d band was fitted first by seven nearest-neighbor parameters P_2 to P_8 which were later reduced to three two-center integrals and one three-center. The success of the narrow-band approximation in Fig. 1 suggests that it may be more significant to introduce two-center integrals for nearest and next-nearest neighbors which are intrinsically of the same order in W, and to ignore three-center ones completely. We note the three-center integrals correspond to crystal field effects, since in the KKR procedure the potential is spherical in each cell. It is interesting that they appear to be so small, at least with a "muffin tin" potential. Incidentally, one can, of course, always do a tight-binding expansion of $E(\mathbf{k})$ and interpret the coefficients as overlap integrals of Wannier functions, but in general these depend on the crystal structure, whereas our orbitals (2) and the two-center overlap integrals are independent of structure. Their variation with distance in different types of strain should therefore always be the same.

In Mueller's[3] model Hamiltonian, the orthogonality coefficients are given by

$$b_{km} = 0.92 j_2(3.8k) Y_{2m}(\mathbf{k}) , \tag{42a}$$

[32] J. L. Beeby and S. F. Edwards, Proc. Roy. Soc. (London) A274, 395 (1963).

which differs radically from what we have estimated from an atomic orbital[33]

$$b_{km} \approx 7.4 j_2(1.2k) Y_{2m}(\mathbf{k}). \qquad (42b)$$

The two agree approximately at low k, but Mueller's cuts off much more rapidly at larger k. Unlike the hybridization matrix elements, the orthogonality terms are not transformed away by (30), and the cause of the discrepancy is a different one. In Mueller's model Hamiltonian the (000), (111), and (200) matrix elements of the potential are treated as constants, independent of k, and this approximation has certainly been found to work quite well in many elements as regards the weak $l=0$ and 1 pseudopotential. However, comparison with (23) and (25) shows that Mueller's potential matrix elements include V_2, the *full* $l=2$ potential, approximately equal and opposite to the orthogonality terms which later largely cancel it. Moreover, this large potential has a strong k dependence, approximately as k^4 in the diagonal element. Since b_{km} varies as k^2, the last two terms of (20) should therefore have the form (in the diagonal matrix elements)

$$-\alpha k^4 + (E - E_d)\beta k^4. \qquad (43)$$

We can write the first term as

$$-\alpha k^4 = -\alpha k_0^4 - \alpha(1 - k_0^4/k^4)k^4, \qquad (44)$$

where k_0 is the value of k where the free-electron parabola crosses E_d. Now the first term in (44) is a constant which can be included with the pseudopotential matrix elements, and the second term included with the second term of (43) to give an effective

$$\beta_{\text{eff}} = \beta - \alpha(1 - k_0^4/k^4)/(E - E_d). \qquad (45)$$

The neglect of the term $-\alpha k^4$ therefore makes the pseudopotential matrix elements algebraically smaller and results in reduced, partially cancelled, orthogonality terms, as found in Mueller's scheme.

The omission of an explicit $-\alpha k^4$ potential term explains another curious aspect of Mueller's results.[34] In his analysis, the $L_1 L_2'$ band gap in the conduction band is largely due to the d-orthogonality terms, i.e., of $l=2$ origin, whereas very simple estimates from atomic data suggest it is largely an s-p splitting. By treating the states L_1, L_2' as purely s and p, respectively, we can estimate the gap by taking simply the difference $A_1 - A_0$ in the well depths of the model potential of Abarenkov and Heine.[35,36] We find[37] 0.30 Ry compared with 0.335 and 0.436 Ry calculated by Burdick[10] and

Segall,[9] respectively. The gap is given by terms

$$V_{0,1}(+) + V_2(-) + (OT)_2(+), \qquad (46)$$

i.e., $l=0$, 1 pseudopotentials, $l=2$ potential, and $l=2$ orthogonality terms, where all three appear to have approximately the same magnitudes and signs shown. By lumping the first two together in a total matrix element $V(111)$ which is small, Mueller finds the gap given largely by the third. However, a more rational interpretation is to group together the last two terms in (46) since they are both $l=2$ and cancel approximately in the usual manner of the OPW cancellation theorem.[22–24] The gap is then exhibited as due to the $l=0,1$ pseudopotential.

IV. HYBRIDIZATION AND THE d BAND

We have emphasized in Sec. I that the shape of the d band is largely determined by the KKR structure constants at energy E_d, while the width of the d band and the hybridization with the conduction band are both determined by the reduced matrix element M, Eq. (6). We shall now exhibit these relations numerically in the band structure of Cu as calculated by Segall,[9] and in the series V to Cu calculated by Mattheiss.[38]

The first step is to calculate M, Eq. (6), which we have done taking the nearest Cu $3d$ orbital at hand,[33] and the Chodorow potential[19] which does not differ substantially from the $l=2$ potential used by Segall.[9] By graphical integration we obtain

$$M = 6.1 \text{ Ry atomic units (a.u.).} \qquad (47)$$

For k along the symmetry directions $\Gamma L(111)$, (Fig. 2), and $\Gamma X(100)$ in the Brillouin zone, only one of the d bands (Λ_1 and Δ_1, respectively) hybridizes with the PW band due to symmetry. These consist of d states with $m=0$ quantized about the direction of $\mathbf{k}$ as axis. The hybridization matrix element therefore is (4)

$$\gamma(\mathbf{k}, m_k = 0)$$

$$= 4\pi N^{1/2} Y_{20}(\theta = 0) \int j_2(kr) V \phi r^2 dr. \qquad (48a)$$

Our k is sufficiently small that we may write $j_2(x) = x^2/15$, and (48a) reduces to

$$(4\pi N/45)^{1/2} k^2 M. \qquad (48b)$$

We have estimated k_0 and $\gamma(k_0)$ from Segall's band structures in the manner of Fig. 2, since the place where the NFE and d bands would cross in the absence of hybridization is a convenient place to discuss γ. The results are shown in Table I and compared with the γ's calculated from (48b) by substituting for k_0. The agreement is satisfactory within the 10% accuracy inherent in reading the curves and in our estimate of M.

[33] B. J. Austin, thesis submitted to University of Cambridge, 1963 (unpublished).
[34] Reference 3, Fig. 2.
[35] V. Heine and I. Abarenkov, Phil. Mag. **9**, 451 (1964).
[36] A. O. E. Animalu and V. Heine, Phil. Mag. (to be published).
[37] I. V. Abarenkov and V. Heine, Tech. Report No. 1, Solid State Theory Section, Cavendish Laboratory, Cambridge, England, 1965 (unpublished).

[38] L. F. Mattheiss, Phys. Rev. **134**, A970 (1964).

TABLE I. Hybridization matrix element at
d-PW crossover.

Direction	k_0	γ (calc.)	γ (Segall)
	a.u.	Ry	Ry
ΓL	0.47	0.080	0.087
ΓX	0.50	0.092	0.105

We now turn to the form of the d bands as determined by (40). In Segall's band structure these may be taken to lie at a mean energy of[9]

$$E_d = 0.35 \text{ Ry} \tag{49}$$

above the bottom Γ_1 of the NFE band. This corresponds roughly to $\epsilon = 0.37$ in the dimensionless units of Ref. 17, which is one of the energies at which the structure constants have been tabulated. With these tables[17] and the appropriate Clebsch-Gordan coefficients[20] we have evaluated the dimensionless constants $(aB_{2m,2m'}/4\pi)$ in (40). The energy levels at Γ, X, and L are given in Table II in terms of $(aB/4\pi)$. They have to be multiplied

TABLE II. Energy levels of d band at symmetry
points in units of $2\pi W/Ka$.

Γ_{12}	$\Gamma_{25'}$	X_1	X_5	X_3
1.71	−0.23	−6.24	3.50	−4.02

X_2	L_1	L_3	L_3
3.03	−6.57	3.12	−0.47

by $2\pi W/Ka$ to give $E-E_d$, where W is given by (12). With the same expansion of the Bessel function as before we have with the use of (6):

$$2\pi W/Ka = (4\pi/225a)K^4M^2. \tag{50}$$

Since the structure constants vary approximately as K^{-4}, it is important in (50) to take $K^2 = 0.315$ Ry corresponding exactly to the $\epsilon = 0.37$ of the structure constants. The final energy levels incorporating (50) and (47) and the addition of (49) are compared with Segall's in Fig. 1. The agreement for the pure d levels (i.e.,
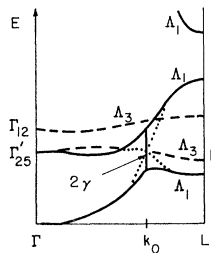

FIG. 2. Band structure of Cu (schematic) along ΓL. Solid line—hybridizing bands; dashed line—pure d bands, dotted line—how the plane wave and Λ_1 d band would cross at k_0 in the absence of hybridization. The hybridization matrix element γ at k_0 would be given exactly by half the gap at the minimum separation of the two bands if γ were a constant. Since γ varies as k^2, the value so obtained is only approximate.

all except L_1, X_1) is remarkably good, except that the width is somewhat too small, which is not surprising in view of our method of estimating M. The important point to note is that increasing M by 9% would result in excellent agreement for *both* the width of the d band *and* the hybridization interaction in Table I, which verifies our assertion that these two quantities are determined by the same parameter.

The levels L_1 and X_1 in Fig. 1 are depressed by an amount $\gamma^2/\Delta E$ because of hybridization with the higher levels of the same symmetry. In Segall's band structure these latter lie at the top of the first band gap in the NFE bands. In our case, (40) corresponds to hybridization with a perfectly free electron band, i.e., in the case of X_1 with a level at $(2\pi/a)^2 = 0.86$ Ry. From Segall's table[9] of energy levels we have that our ΔE is 0.690 Ry compared with his 1.055 Ry. The total amount of hybridization can be estimated[39] as 0.072 Ry for Segall, which incidentally is enough to depress X_1 from above X_3 in a pure d band, to below X_3. Our hybridization should therefore be about 0.038 Ry larger. Moving our X_1 level up by that amount would restore its position relative to X_3 nicely the same as for Segall. A similar argument may be applied to L_1, where the effect is even larger because the L_1 NFE level lies lower.

It is illuminating to consider the over-all width of the d band from a cruder point of view derived from the cellular method for band-structure calculations. We expect the lowest energy state in the d band to have bonding character between nearest neighbors. Indeed, we find this to be so in the $x=0$ plane if we form a tight-binding function with atomic orbitals of yz symmetry for the X_3 level at $k = (2\pi/a)(1,0,0)$ which in the absence of hybridization lies lowest in the band.[40] We would therefore expect in the spirit of a Wigner-Seitz calculation that its energy corresponds approximately to the boundary condition

$$(d\psi/dr)_R = 0, \tag{51a}$$

applied to the $l=2$ radial function at the radius R of the inscribed sphere. One might argue whether to use the mean atomic radius instead of R, but the angular functions concentrate the orbitals in specific directions and R, half the nearest-neighbor distance, is probably what is relevant here. Similarly, the level X_5 at or near the maximum of the d band is given by the antibonding boundary condition

$$\psi(R) = 0. \tag{51b}$$

Now the wave function at and beyond R is completely determined by the phase shift (1) according to Eq. (A3) of the Appendix, and we can calculate the energies

[39] Reference 3, Figs. 6 and 7. Note, however, that these really refer to the Burdick band structure, but that the hybridization is nearly the same for **k** near the zone faces (Ref. 3, Table III).
[40] Reference 3, Fig. 6.

which give (51),

$$E_{max} - E_d = -\tfrac{1}{2}W(n_2(KR)/j_2(KR)),$$

$$E_{min} - E_d = -\tfrac{1}{2}W(n_2'(KR)/j_2'(KR)). \qquad (52)$$

We again expand the Bessel functions and obtain for the width Δ of the d band without hybridization

$$\Delta = E_{max} - E_{min} = 56.25W(KR)^{-5}. \qquad (53)$$

This result can be simplified by substituting for W from (12) and (6);

$$\Delta = \tfrac{1}{2}M^2R^{-5}. \qquad (54)$$

We obtain from (54) $\Delta = 0.227$Ry, in unexpectedly good agreement with $X_5 - X_3 = 0.226$Ry calculated (Fig. 1) with the KKR constants for the same value of M. The closeness of agreement must be regarded as fortuitous, since Wood[41] for example found the $3d$ bandwidth of iron to be 15% greater in the bcc phase than in the fcc with essentially the same potential, so our formula can only be approximate. We note from (54) that Δ is independent of K, i.e., of how high above Γ_1 the d band lies. In this regard it behaves like a conventional tight-binding band, and the resonance effects which depend on K all cancel out. The prediction of (54) that the bandwidth should decrease as R^{-5} on expanding the lattice appears to be in close agreement with the results of actual band structure calculations.[13]

TABLE III. Bandwidth and hybridization in the $3d$-transition series, after Ref. 38.

	V	Cr	Fe	Co	Ni	Cu
Δ(Ry)	0.49	0.50	0.38	0.32	0.29	0.21
γ(Ry)	0.24	0.24	0.20	0.15	0.14	0.11
k_0(a.u.)	0.64	0.65	0.69	0.62	0.61	0.57
Structure	bcc	bcc	bcc	fcc	fcc	fcc
Eq. (55)	1.4	1.4	1.9	2.2	2.1	1.9

We can use (54) to trace the relationship between hybridization and bandwidth in the series of metals V to Cu. The values of γ and k_0 (Fig. 2), as read off from the band structures,[38] are shown in Table III. Elimination of M between (48b) and (54) gives

$$\Delta k_0^4NR^5/\gamma^2 = 45/8\pi = 1.79. \qquad (55)$$

The left side of (55) is also given in Table III, and is reasonably constant about the predicted value, whereas Δ for example varies by a factor of 2.4 between Cr and Cu. It is not clear whether the remaining discrepancy is real, or comes from the manner of reading γ from the curves as described in Fig. 2, or from the fact that the $E(k)$ were calculated only at three intermediate values[42] of k between 0 and $2\pi/a$. In particular, the low values of the product (55) for V and Cr are puzzling, since the

bcc structure tends to give a larger Δ than the fcc, as already remarked.

APPENDIX

Our purpose is to prove that the Hamiltonian matrix $H_{mm'}(\mathbf{k})$ calculated with the "tight-binding" basis set (41) leads directly to the secular equation (40).

Φ in (2) is the solution of

$$(-\nabla^2 - E_d)\Phi = -V(\mathbf{r})\Phi \qquad (A1)$$

and can be written

$$\Phi(\mathbf{r}) = \Phi(\text{free}) + \int G_0(\mathbf{r,r'})V(\mathbf{r'})\Phi(\mathbf{r'})d\mathbf{r'}, \qquad (A2)$$

where $\Phi(\text{free})$ is the free-space "unperturbed" wave function. The two terms are exhibited explicitly in[43] KR (A3.2)

$$\Phi_m(\mathbf{r}) \sim A[j_2(Kr) - \tan\eta_2 n_2(Kr)]Y_{2m}(\mathbf{r}), \qquad (A3)$$

and since at the resonance $\eta_2 = \tfrac{1}{2}\pi$, the first term is negligible compared with the second and we drop it from (A2). G_0 is given by KR Eq. (A2.2) but we need it in the slightly different form

$$G_0(\mathbf{r,r'}) = -(N/M)\sum_\kappa \frac{\exp i\boldsymbol{\kappa}\cdot(\mathbf{r-r'})}{\kappa^2 - E_d} \qquad (A4)$$

appropriate to periodic boundary conditions in a box of M cells and total volume M/N. We therefore have from (A2) in the notation of (41)

$$\Phi_m(\mathbf{r};\mathbf{s}) =$$

$$-\frac{N}{M}\int\sum_\kappa \frac{\exp i\boldsymbol{\kappa}\cdot(\mathbf{r-r'-s})}{\kappa^2 - E_d}V(\mathbf{r'})\phi_m(\mathbf{r'})d\mathbf{r'}, \qquad (A5)$$

where using (2a) we have written ϕ_m instead of Φ_m on the right since V extends only to radius R. The factor $\exp -i\boldsymbol{\kappa}\cdot\mathbf{s}$ comes from centering the Φ_m at $\mathbf{s}$.

Down the diagonal of $H_{mm'}$ we have of course $E_d\delta_{mm'}$ and we now calculate the two center terms

$$\sum_\mathbf{s}{}' \exp i\mathbf{k}\cdot\mathbf{s}\langle\Phi_m(0)|V(0)|\Phi_{m'}(\mathbf{s})\rangle. \qquad (A6)$$

Here the term $s=0$ is excluded. Let us temporarily include it and subtract it out later. As before, we can replace $\Phi_m(\mathbf{r},0)$ in (A6) by $\phi_m(\mathbf{r})$ because the V term

[41] J. H. Wood, Phys. Rev. **126**, 517 (1962).
[42] L. F. Mattheiss (private communication).
[43] We denote in this way the equations of Ref. 8.

operates only in cell zero, and we substitute (A5) for $\Phi(s)$. Equation (A6) then becomes

$$-\frac{N}{M}\int\int \sum_s \sum_\kappa \exp i(\mathbf{k}-\boldsymbol{\kappa})\cdot\mathbf{s}\frac{\exp i\boldsymbol{\kappa}\cdot(\mathbf{r}-\mathbf{r}')}{\kappa^2-E_d}\phi_m(\mathbf{r})$$

$$\times V(\mathbf{r})V(\mathbf{r}')\phi_m(\mathbf{r}')d\mathbf{r}d\mathbf{r}'. \quad (A7)$$

The summation over $\mathbf{s}$ gives zero unless $\mathbf{k}-\boldsymbol{\kappa}$ is some reciprocal lattice vector $\mathbf{g}$ in which case it gives M. The central part of (A7) becomes therefore

$$-N\sum_{\mathbf{g}}\frac{\exp i(\mathbf{k}+\mathbf{g})\cdot(\mathbf{r}-\mathbf{r}')}{(\mathbf{k}+\mathbf{g})^2-E_d}, \quad (A8)$$

which is just the Green function $G(\mathbf{r},\mathbf{r}')$ of Ref. 8. We now note from KR Eqs. (A2.21), (A2.2) that the $\mathbf{s}=0$ term of G which we have to subtract out is just G_0, and from KR Eq. (A2.1) that $G-G_0=D$, whence (A7) becomes

$$\int\int D(\mathbf{r},\mathbf{r}')\phi_m{}^*(\mathbf{r})V(\mathbf{r})V(\mathbf{r}')\phi_{m'}(\mathbf{r}')d\mathbf{r}'d\mathbf{r}. \quad (A9)$$

The expansion KR Eq. (A2.3) and our Eq. (12) show (A9) is equal to

$$A_{2m,2m'}(W/2K), \quad (A10)$$

from which (40) follows.[44]

The proof is incomplete in two respects. First we have assumed implicitly that $\psi_{\mathbf{k}m}$ is normalized correctly to unity. It is clear from (2b) that $\int|\Phi_m|^2 d\mathbf{r}$ diverges but only as the cube root of the volume. It is easy to verify that $\int|\psi_{\mathbf{k}m}|^2 d\mathbf{r}$ on the other hand is finite. This follows from (41) and (A5), and again using the summation on $\mathbf{s}$ to restrict $\boldsymbol{\kappa}$ to $\mathbf{k}+\mathbf{g}$. We obtain for the norm

$$\sum_{\mathbf{g}}\left|\frac{\gamma_{\mathbf{k}+\mathbf{g},m}}{(\mathbf{k}+\mathbf{g})^2-E_d}\right|^2. \quad (A11)$$

What is not clear is that this is nearly unity. We conclude that there must be sufficient destructive interference among all the tails of the $\Phi_m(\mathbf{r},\mathbf{s})$ to eliminate the infinity, but they can and do still give a finite contribu-

tion. The norm of $\psi_{\mathbf{k}m}$ is $M|\psi_{\mathbf{k}m}|^2$ integrated over one cell, say the zeroth one. In that cell we expect $\psi_{\mathbf{k}m}$ to be approximately equal to ϕ_m but it cannot be exactly equal if for no other reason than that $\psi_{\mathbf{k}m}$ must vary with $\mathbf{k}$. The difference is in fact the sum of the tails from the other centers and hence of order $W^{1/2}$. Its functional form is the sum of plane waves and hence the $l=2$ component is proportional to $j_2(Kr)$ in any cell. We therefore write in cell zero

$$\psi_{\mathbf{k}m}-\phi_m\sim W^{1/2}j_2(Kr), \quad (A12)$$

and the normalization only adds terms of order $W^{3/2}$ through the two-center integrals.

Finally there are the three-center integrals which together may be written

$$\int|\psi_{\mathbf{k}m}-\phi_m|^2 V(\mathbf{r})d\mathbf{r}, \quad (A13)$$

the integration being over cell zero again. (We include among the three-center integrals the special term $\langle\Phi(s)|V(0)|\Phi(s)\rangle$.) We have already noted from (3) and (4) that the two-center integrals are of order W, and we may write their sum as

$$\int\phi_m V(\psi_{\mathbf{k}m}-\phi_m)d\mathbf{r}=O(W). \quad (A14)$$

Since from (A12), $\psi-\phi\to 0$ as $W\to 0$, (A13) tends to zero faster than (A14), i.e., is negligible to order W. There is at first sight a slight paradox here. If we substitute (A12) directly into (A13) we have

$$W\int[j_2(Kr)]^2 V(r)4\pi r^2 dr, \quad (A15)$$

and might suppose the integral to be of order unity, i.e., the three-center terms to be of order W. However, the transition matrix element $W^{1/2}$ tending to zero demands that V be concentrated more and more closely to the origin, and the integral in (A15) tends to zero because $[j_2(Kr)]^2$ varies as r^4. The same argument explaines why (6) is $O(W^{1/2})$ and not $O(1)$.

We have therefore derived (40) from a conventional "tight-binding" calculation applied to the overlapping resonance orbitals Φ, only the two-center integrals contributing to lowest order W in the bandwidth.

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[44] The A's and B's differ only in the convention chosen for the angular factors Y_{lm}. See Refs 8 and 17.