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Electronic structure of transition metals. III. d-band resonance and Regge-pole theory*

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This is the third paper in our current series on the electronic structure and properties of the transition metals in the pseudopotential approximation. Here we review, reformulate, and generalize the resonance model of s-d hybridization in one-electron energy bands so as to be applicable to scattering processes at arbitrary energies different from the eigenvalues of the one-electron wave equation in a crystal. This is achieved by formulating the resonance model in two ways, first in the framework of the one-electron energy-band secular equation given by the Korringa-Kohn-Rostoker (KKR) method in Ziman's "plane-wave representation," and second as a scattering problem in terms of standard partial-wave phase-shift analysis. The former leads to a *real* resonance energy, say E_d, while the latter leads to a *complex* resonance energy, say $E_d+\frac{1}{2}iW$ where W is a measure of s-d interaction which also determines the d bandwidth. To relate E_d and W, and hence determine W in the framework of the KKR or any other valid transition-metal pseudopotential form factor, the scattering problem is reformulated in *complex angular momentum representation* using the Regge-pole theory in nonrelativistic potential scattering; the result, $W\propto(dE/dl)_{l=2}$, is then interpreted in the context of the transition-metal-model-potential form factor discussed in the first two papers of this series and the quantitative predictions are compared with the results of augmented-plane-wave one-electron energy-band calculation and those of the renormalized-atom method, and with recent photoemission data. The agreement between the various results is systematically good for transition metals of the 3d, 4d, and 5d series, as far as the results are known.

I. INTRODUCTION

In this (third) paper of our current series[1,2] on the electronic structure and properties of the transition metals in the pseudopotential approximation, we shall review, reformulate, and generalize the resonance model[3–5] of s-d hybridization in transition metals. The conceptual problem of relating the parameters of the resonance model to the d-band position (E_d) and d bandwidth (Δ), which is presently formulated in terms of the solutions of the one-electron energy-band secular equation, will be reformulated from the point of view of formal scattering theory based on partial-wave analysis[6] in complex angular momentum representation and the concomitant Regge-pole theory.[7,8] The Regge-pole theory will elucidate the resonance model by providing a model-independent relation between the real and the imaginary parts of the complex resonance energy $E_d+\frac{1}{2}iW$ defined by the pole of the partial-wave amplitude for s-d scattering in the neighborhood of the $l=2$ resonance, in the complex energy plane. This model-independent relation may be used to deduce the parameters of the resonance model from any valid transition-metal pseudopotential form factor, in particular, the transition-metal-model-potential (TMMP) form factor discussed in the first two papers[1,2] of this series, which will provide a basis for the determination of the two parameters from the systematics of the atomic spectroscopic data.[9]

In the context of the one-electron energy-band secular equation given by the Korringa-Kohn-Rostoker (KKR) method[10] or equivalently the augmented-plane-wave (APW) method,[11] s-d hybridization is the terminology used to refer to the crossover of the nearly-free-electron (NFE) s band and the tight-binding d-band complex in the transition (including noble) metals. Heine (Ref. 4, Fig. 2) has defined a hybridization matrix element, which determines all two-center integrals proportional to the d bandwidth Δ, as one-half the minimum separation between the s-band and the d-band complex at the crossover region. The d-band position E_d is located at the center of the crossover region in the d-band complex, in such a way that Δ is an approximate measure of the gap that opens up at the crossover region as a result of s-d hybridizing interaction. Ziman[3] was the first to suggest that this type of hybridization would be produced by the lowest-order secular equation in the KKR method, if the $l=2$ partial-wave component of the KKR pseudopotential form factor [proportional to $\tan\eta_2'$, defined in Eq. (8)] is parameterized by a phase shift having the resonance form, $\eta_2=\tan^{-1}[\frac{1}{2}W/(E_d-E)]$, where $W\propto\Delta$. A brief review of Ziman's formulation of the resonance model will be given in Sec. II A.

As in the orthogonalized-plane-wave (OPW) pseudopotential method,[12] the effective-potential form factors associated with the KKR and the APW methods are called phase-shift pseudopotentials,[13,14] and the pseudopotential interpretation is introduced with the objective of constructing detailed theories of electron-phonon interaction, of electron-impurity interaction, of cohesion, etc., in the diffraction model.[12] For this reason, in the phase-shift pseudopotential program, we are faced with the question[13]: how should we set about the extrapolation of the phase shifts determined, for example, at the Fermi surface,[14] to arbitrary energies (appropriate to scattering problems) which are no longer eigenvalues of the one-electron wave equation in a periodic potential?

This brings us to the formulation of s-d hybridization as a scattering problem, which is discussed in the framework of the KKR pseudopotential form factor in Sec. II B. The basic idea is to generalize the relatively well-understood problem of a single transition-metal impurity, such as a copper atom, placed in a free-electron gas, to the realistic problem of scattering from a periodic lattice of transition-metal atoms sitting in a neutralizing background of the valence-electron gas. For a single impurity, s-d interaction is formulated so as to answer the question: How does a single electron prepared in the localized d state of the transition-metal impurity atom leak out (into an s state of the surrounding free-electron gas)? This is not an eigenvalue problem, but a tunneling or scattering problem. Consequently, the energy, say E_d'', of the d state obtained by integrating the one-electron Schrödinger equation subject to the boundary condition appropriate for a propagating exponentially damped s wave far away from the impurity atom need not be a real energy.[15] In fact, E_d'' is a complex energy: its imaginary part (W) is inversely proportional to the lifetime of the d state (before it decays into the s state) and therefore is a measure of the strength of s-d interaction. The d bandwidth (Δ) arises out of the interference of such resonances on many sites and in simple models,[16] Δ is proportional to W.

In Sec. III, the scattering point of view (developed in Sec. II B) will be reformulated in the complex-angular-momentum representation using the Regge-pole theory, from which the relation between the real and the imaginary parts of the complex resonance energy will be deduced from the analytical properties of the Regge trajectories. In Sec. IV, this model-independent relation will be used to interpret the resonance model in the framework of any valid transition-metal form factor, in particular the TMMP form factor, and the predictions of the TMMP method will be compared with results derived from the APW method and the renormalized-atom method.[16] Comparison of results with recent photoemission data[17] will be made in Sec. V and the paper will be concluded in Sec. VI.

II. RESONANCE MODEL IN ENERGY BAND AND SCATTERING THEORIES

We have two objectives in this section. The first is to review the resonance model of s-d hybridization in transition-metal energy bands; and the second is to present a natural generalization of this model to scattering problems in the frame-work of the KKR or equivalently the APW or phase-shift pseudopotential concept.

A. *s-d* hybridization and band theory

The original formulation of the resonance of s-d hybridization by Ziman[3] was based on a rigorous painstaking transformation of the KKR secular equation into a "plane-wave representation." The result was subsequently derived more simply from the familiar APW method by Morgan[3] whose approach we shall adopt in this review; and further elucidation of the results was given by Heine[4] and others.[5] The objective of the resonance model was to relate the structure of the s-d band crossing to the phase-shifts produced by the true muffin-tin potential or the equivalent phase-shift pseudopotential: the true phase shifts will be denoted by η_l ($l=0,\ 1,2,\ldots$) and the effective (pseudo) phase shifts will be denoted by η_l'. The resonance model was formulated in terms of η_l by Ziman[3] and in terms of η_l' by Heine[4]; but irrespective of which phase shift one uses, the essential point we wish to emphasize is that the resonance model has been introduced in an entirely *ad hoc* manner (by looking at the answer); in fact, the existence of such a resonance in the framework of a one-electron energy eigenvalue problem based on a Hermitian Hamiltonian is pathological, as we shall see below in Sec. II B.

We start from the secular equation for one-electron energy bands in the APW method[11] (in units such that $\hbar = 2m = 1$):

$$\det\|[(\vec{k}-\vec{g}_n)^2 - E]\delta_{nn'} + V^{\text{APW}}(\vec{k}-\vec{g}_n, \vec{k}-\vec{g}_{n'})\| = 0, \quad (1)$$

where the APW pseudopotential form factor is defined for arbitrary states, $\vec{k}$ and $\vec{k}'$ by

$$V^{\text{APW}}(\vec{k},\vec{k}') = \frac{4\pi R^2}{\Omega_0}\Bigg((E - \vec{k}\cdot\vec{k}')j_1(|\vec{k}-\vec{k}'|R)/|\vec{k}-\vec{k}'| + \sum_{l=0}^{\infty}(2l+1)P_l(\cos\theta_{\vec{k}\vec{k}'})j_l(kR)j_l(k'R)\frac{\chi_l'(R,E)}{\chi_l(R,E)}\Bigg). \quad (2)$$

In these equations, $\chi_l(R,E)$ and $\chi_l'(R,E) \equiv (d\chi_l/dr)$ are, respectively, the radial wave function and its derivative (evaluated at $r=R$); j_l is the spherical Bessel function; $P_l(\cos\theta_{\vec{k}\vec{k}'})$ is the Legendre's polynomial with argument $\cos\theta_{\vec{k}\vec{k}'}$, where $\theta_{\vec{k}\vec{k}'}$ is the angle between $\vec{k}$ and $\vec{k}'$; R is the radius of the muffin-tin potential in the crystal; and Ω_0 is the unit cell volume, for a monoatomic crystal lattice.

The actual lattice potential appears implicitly in the secular equation through the logarithmic derivative of the radial wave function determined by the radial-wave equation

$$-\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\chi_l}{dr}\right)+\left(\frac{l(l+1)}{r^2}+V(r)\right)\chi_l=E\chi_l\ , \tag{3}$$

where $V(r)$ is the muffin-tin potential associated with a single lattice site in the crystal. By matching χ_l to the corresponding free-space waves outside each muffin-tin sphere, the effect of V can be simulated through the phase shifts $\eta_l \equiv \eta_l(E)$ defined by the standard relation

$$\beta_l \equiv \frac{\chi_l'(R,E)}{\chi_l(R,E)}=\frac{j_l'(\kappa R)-\tan\eta_l n_l'(\kappa R)}{j_l(\kappa R)-\tan\eta_l n_l(\kappa R)}\ , \tag{4}$$

where $\kappa^2 = E$, and j_l, n_l are, respectively, the spherical Bessel and Neumann functions, with derivatives, $j_l'(\kappa R) = dj_l/dr$ and $n_l'(\kappa R) = dn_l/dr$, evaluated at $r = R$.

Now, in an "empty lattice," all phase shifts must vanish. However, we observe that making all $\eta_l = 0$ does not cause all coefficients

$$[V^{\mathrm{APW}}(\vec{\mathrm{k}}-\vec{\mathrm{g}}_n, \vec{\mathrm{k}}-\vec{\mathrm{g}}_{n'}]^0 \equiv \frac{4\pi R^2}{\Omega_0}\left([E-(\vec{\mathrm{k}}-\vec{\mathrm{g}}_n)\cdot(\vec{\mathrm{k}}-\vec{\mathrm{g}}_{n'}]\frac{j_1(|\vec{\mathrm{g}}_n-\vec{\mathrm{g}}_{n'}|R)}{|\vec{\mathrm{g}}_n-\vec{\mathrm{g}}_{n'}|} + \sum_{l=0}^{\infty}(2l+1)P_l(\cos\theta_{nn'})j_l(|\vec{\mathrm{k}}-\vec{\mathrm{g}}_n|R)j_l(|\vec{\mathrm{k}}-\vec{\mathrm{g}}_{n'}|R)\frac{j_l'(\kappa R)}{j_l(\kappa R)}\right) \tag{5}$$

to vanish. Thus, the simple solution $E(k) = k^2$ requires detailed computation involving in principle all values of l, $\vec{\mathrm{g}}_n$, and $\vec{\mathrm{g}}_{n'}$. For this reason, it was not obvious when the APW method was first used that simple metals, like Al and Pb should have NFE energy bands.

If we make use of the relation

$$j_l(x)\frac{dn_l(x)}{dx}-n_l(x)\frac{dj_l(x)}{dx}=\frac{1}{x^2}\ , \tag{6}$$

then it may be verified that

$$\chi_l'/\chi_l = j_l'/j_l - \tan\eta_l'/\kappa(Rj_l)^2\ , \tag{7}$$

where

$$\cot\eta_l' = \cot\eta_l - n_l(\kappa R)/j_l(\kappa R)\ . \tag{8}$$

Consequently, if we define the KKR form factor by the relation

$$V^{\mathrm{KKR}} = V^{\mathrm{APW}} - (V^{\mathrm{APW}})^0\ , \tag{9}$$

then we find Ziman's secular equation[3] for the KKR method

$$\det\|[(\vec{\mathrm{k}}-\vec{\mathrm{g}}_n)^2-E]\delta_{nn'}+V^{\mathrm{KKR}}(\vec{\mathrm{k}}-\vec{\mathrm{g}}_n, \vec{\mathrm{k}}-\vec{\mathrm{g}}_{n'})\| = 0\ , \tag{10}$$

in which

$$V^{\mathrm{KKR}}(\vec{\mathrm{k}},\vec{\mathrm{k}}') \equiv -\frac{4\pi}{\Omega_0\kappa}\sum_{l=0}^{\infty}(2l+1)\tan\eta_l' \times \frac{j_l(kR)j_l(k'R)}{[j_l(\kappa R)]^2}P_l(\cos\theta_{\vec{\mathrm{k}}\vec{\mathrm{k}}'})\ . \tag{11}$$

The identity in Eq. (9) shows that Ziman's form of the KKR method does not involve any new approximation in the APW method if the zero of the muffin-tin potential is fixed by this identity in the two methods.

On the basis of Eq. (8), Ziman has noted that one the s-band in transition metals if one sets $\vec{\mathrm{g}}_n = \vec{\mathrm{g}}_{n'}$ $= 0$ in Eq. (10) and

$$\tan\eta_2 = \tfrac{1}{2}W/(E_d - E)\ . \tag{12}$$

For in this circumstance one then finds, from Eq. (8),

$$\tan\eta_2' = \tfrac{1}{2}W/(E_d' - E)\ ; \tag{13}$$

and from Eqs. (10) and (11),

$$E = k^2 - \frac{20\pi}{\Omega_0\kappa}\tan\eta_2' \equiv k^2 - \frac{10\pi}{\Omega_0\kappa}\frac{W}{E_d'-E}\ , \tag{14}$$

where

$$E_d' = E_d - \tfrac{1}{2}W[n_2(\kappa R)/j_2(\kappa R)] \tag{15}$$

defines a shifted energy, corresponding to the point where η_2' goes through $\frac{1}{2}\pi$. When Eq. (13) is solved for real k, the result would look as if a free-electron band had crossed a single d level and "hybridized" with it. The form in Eq. (12) is just the way the $l = 2$ partial-wave phase shift will behave if the hybridization is pictured as a resonance of a free-electron s wave with a localized d wave to form a virtual bound state. For this reason, Ziman's conjecture was christened the resonance model and has subsequently been investigated further by Heine[4] and others.[5]

The d-band width (Δ) is given in this type of simplified model of s-d hybridization by [cf. Eqs. (17) and (18) of Ref. 16]

$$\Delta = \tfrac{1}{2}W(n_2'(\kappa R)/j_2'(\kappa R) - n_2(\kappa R)/j_2(\kappa R))\ . \tag{16}$$

This is proportional to W.

In the APW method, the quantity frequently calculated is not η_l' but the function β_l related to η_l' via Eqs. (4) and (8) by

$$\cot\eta_l' = \frac{n_l'(\kappa R)-\beta_l n_l(\kappa R)}{j_l'(\kappa R)-\beta_l j_l(\kappa R)} - \frac{n_l(\kappa R)}{j_l(\kappa R)}\ . \tag{17}$$

Thus, η_l' goes through $\frac{1}{2}\pi$ if β_l becomes infinite at some energy: this requires a node in the radial

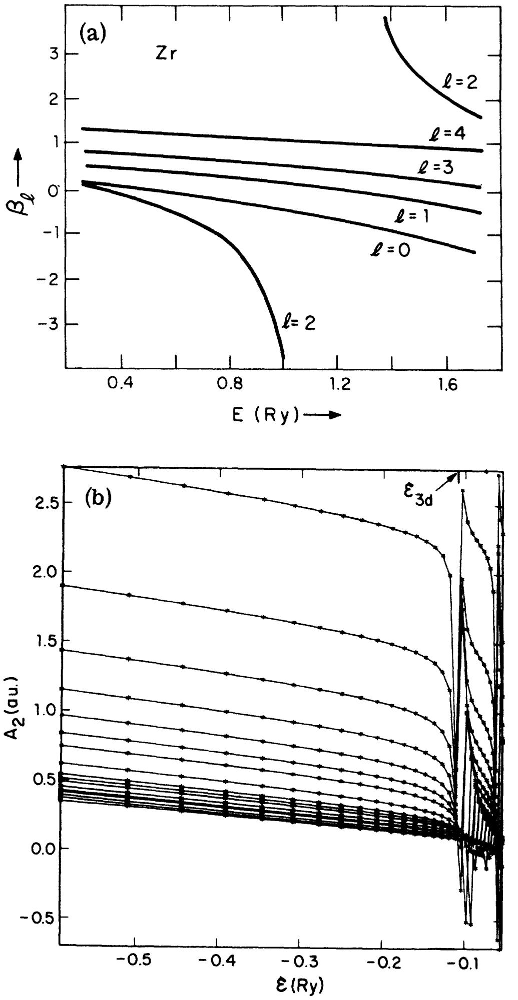

FIG. 1. (a) Energy dependence of the logarithmic derivative of the radial wave function derived from Eq. (3) in the APW method, $\beta_l(E) \equiv \chi_l'(R,E)/\chi_l(R,E)$ (after Loucks, Ref. 11, Fig. 3–11 for zirconium). (b) Energy dependence of the model potential parameter $A_2(\mathcal{E})$ for all values of the model radius R_m between 2.0 and 15.0 a.u.) discussed in Ref. 1, showing the d-band resonance at $\mathcal{E}=\mathcal{E}_{3d}$ and its apparent independence of the choice of R_m. (R_m decreases from 2.0 at the top to 15.0 at the bottom, and the chemical valence is assumed to be unity for simplicity.)

wave function at $r=R$. The practical aspects of the APW method shown in Fig. 1(a) indicate that β_l does go through infinity for $l=2$ at some energy; the analog of this in the TMMP method is the behavior of the model potential parameter A_l for $l=2$, which is illustrated in Fig. 1(b) for comparison. We shall return to the significance of this analogy in Sec. IV.

It is also of interest to note that the expression for Δ in Eq. (16) results from Eq. (13) by setting

$$\Delta \equiv E_d' - E_0 = \tfrac{1}{2} W \cot\eta_2'(E_0) , \qquad (18)$$

where E_0 is the energy at which $\beta_2=0$ in the expression (17) for $\cot\eta_2'$. Thus in the resonance model, the limits $\beta_2=\infty$, and $\beta_2=0$ determine, respectively, the position and the width of the d band in the APW method.

B. Generalization to resonance scattering

The purpose of the pseudopotential interpretation of the result of the KKR method is to generate a form factor, $V^{\rm KKR}(\vec{k},\vec{k}')$ which can be used not only for energy band calculations but also for calculating the transport properties of the transition metals, such as the electrical resistivity of liquid transition metals (to be reported in Paper IV of this series). It turns out, however, that $V^{\rm KKR}(\vec{k},\vec{k}')$ cannot be used for the calculation of transition probability for various scattering processes, because the contribution from the $l=2$ partial wave to the transition rate is proportional to $|\tan\eta_l'|^2$ which is divergent when $E=E_d'$.

In order to obtain a finite contribution from the $l=2$ resonance, we have to generalize $V^{\rm KKR}(\vec{k},\vec{k}')$ of Eq. (11) to a T-matrix pseudopotential form factor constructed from the phase shifts η_l':

$$T^{\rm KKR}(\vec{k},\vec{k}') = -\frac{4\pi}{\Omega_0\kappa}\sum_{l=0}^{\infty}(2l+1)e^{-i\eta_l'} \times \sin\eta_l' \,\frac{j_l(kR)\,j_l(k'R)}{[j_l(\kappa R)]^2}\, P_l(\cos\theta_{\vec{k}\vec{k}'}) . \qquad (19)$$

This expression has the same functional form as $V^{\rm KKR}(\vec{k},\vec{k}')$; and since $j_l(kR)j_l(k'R)/[j_l(\kappa R)]^2=1$ on the energy shell $k=k'=\kappa$, the expression (with η' replaced by $-\eta'$) simulates the standard form of the T matrix for elastic scattering.

The similarity between $V^{\rm KKR}$ and $T^{\rm KKR}$ may be accentuated by *defining* an effective *scattering phase shift* δ_l' so that

$$\tan\delta_l' \equiv e^{-i\eta_l'}\sin\eta_l' . \qquad (20)$$

Then, for $l=2$, we find

$$\tan\delta_2' = \tfrac{1}{2} W/(E_d'' - E) , \qquad (21)$$

where

$$E_d'' = E_d' + \tfrac{1}{2} iW \qquad (22)$$

corresponds to a complex resonance energy. On comparing Eq. (21) with Eq. (13), we see that resonance occurs in s-d scattering when the s-electron energy (E) is nearly equal to the d-electron energy (E_d') and the lifetime of the resonance is inversely proportional to W, as expected.

The practical significance of this result may be summarized as follows. The phase shifts η_l' are, in principle, known *real* functions at a fixed energy, say, $E=E_F$ of a Bloch one-electron state in the crystal. As in ordinary (simple-metal) pseudopotential theory,[12] the differences between η_l' and the effective scattering phase shifts δ_l' on the Fermi surface ($E = E_F$) may be neglected for all nonresonant ($l \neq 2$) states, so that we may ignore the differences between the V matrix of Eq. (11) and the T matrix of Eq. (19), by taking the form factor to be *real* as in Eq. (11). For the resonant ($l = 2$) state, we have to define $\tan\eta_2'$ in Eq. (11) so that

$$\begin{aligned} \tan\eta_2' &= \tfrac{1}{2} W/(E_d' - E) && \text{for energy bands} \\ &= \tfrac{1}{2} W/(E_d' - E + \tfrac{1}{2} iW) && \text{for scattering .} \end{aligned} \tag{23}$$

For this reason, the most practical form of the KKR form factor which emphasizes the analytical structure of the resonance state in the calculation of transition rates for scattering on the Fermi surface is

$$\tilde{V}^{\text{KKR}}(\vec{k}, \vec{k}') = (4\pi/\Omega_0) \sum_{l=0}^{\infty} (2l+1) T_l P_l(\cos\theta_{\vec{k}\vec{k}'}) \; , \tag{24}$$

where

$$T_l = -\kappa^{-1} \tan\eta_l' \frac{j_l(kR)\, j_l(k'R)}{[j_l(\kappa R)]^2} \quad \text{for } l \neq 2 \tag{25}$$

and

$$T_2 = -\kappa^{-1} \frac{\frac{1}{2} W}{E_d' - E + \frac{1}{2} iW} \frac{j_2(kR)\, j_2(k'R)}{[j_2(\kappa R)]^2} \tag{26}$$

are the partial-wave amplitudes given by Eq. (11) for $l \neq 2$ and by Eq. (19) for $l = 2$.

There is no loss in generality in considering $\tilde{V}^{\text{KKR}}(\vec{k}, \vec{k}')$ rather than the V matrix or the T matrix. The main advantage of $\tilde{V}^{\text{KKR}}(\vec{k}, \vec{k}')$ will be realized in practical applications (to be reported in Paper IV of this series) in which the nonresonant ($l \neq 2$) contributions to the formal expansion in Eq. (24) will be represented by a *real* model potential form factor. In this way the truncation errors that necessarily arise in current applications of the complete T-matrix form factor to calculation of electronic properties[14] will be eliminated. From this perspective, the lengthy analysis presented in this section is seen to serve as the formal mathematical framework underlying the transition-metal-model-potential approximation.

III. COMPLEX-ANGULAR-MOMENTUM REPRESENTATION

Having shown in Sec. II that the KKR method leads to a scattering T-matrix pseudopotential form factor at or near the $l = 2$ resonance in transition metals, it is now straightforward to relate E_d' and W through the analytical properties of the partial-wave amplitude in the framework of formal scattering theory. To this end, we shall work in the complex-angular-momentum representation first introduced by Regge in nonrelativistic potential scattering theory.[7,8] The general philosophy of the Regge-pole theory is quite simple, and we shall begin by presenting the key results of the theory before delving into the pertinent details.

Two basic steps are involved. The first is simply to express the partial-wave amplitude defined by Eq. (26) in the form

$$\frac{\frac{1}{2} W}{E_d' - E + \frac{1}{2} iW} \equiv \frac{\gamma_l}{\alpha(E) - l} \bigg|_{l=2} \; . \tag{27}$$

Here $\alpha(E)$ is a complex-angular-momentum variable—a function of the *real* energy parameter, E; l is the usual real-angular-momentum quantum number; and γ_l is to be determined. The net effect of the change to the complex-angular-momentum representation is to transfer the pole at $E = E_d' + \frac{1}{2} iW$ in the complex energy plane to a pole at

$$\operatorname{Re}\alpha(E_d') = l \equiv 2 \; , \tag{28}$$

in the complex angular momentum plane. The latter is called a "Regge pole"; and the function, $\operatorname{Re}\alpha(E)$ vs E, defines the corresponding "Regge trajectory."[18,19] No approximation is involved in Eq. (27).

The second basic step, which goes beyond the present status of Ziman's theory, is to relate E_d' and W via the analytical properties of the Regge trajectory by expanding $\alpha(E)$ about the energy $E = E_d'$. Then Eq. (27) becomes

$$\tfrac{1}{2} W/(E_d' - E + \tfrac{1}{2} iW) \equiv \gamma_d / [(E_d' - E)\alpha' + i \operatorname{Im}\alpha] \; , \tag{29}$$

where $\alpha' \equiv (d\alpha/dE)_d$, and we have used Eq. (28) to get $\alpha(E_d') - l = i \operatorname{Im}\alpha(E_d')$. The right-hand side of Eq. (29) may be rewritted *exactly* in the form

$$\frac{\gamma_d}{(E_d' - E)\alpha' + i\operatorname{Im}\alpha} = \frac{\gamma_d/\alpha'}{E_d' + \Delta E_d' - E + \frac{1}{2} iW} \; , \tag{30}$$

where

$$\begin{aligned} \Delta E_d' &= \operatorname{Im}\alpha \operatorname{Im}\alpha' / [(\operatorname{Re}\alpha')^2 + (\operatorname{Im}\alpha')^2] \; ; \\ W &= 2 \operatorname{Im}\alpha \operatorname{Re}\alpha' / [(\operatorname{Re}\alpha')^2 + (\operatorname{Im}\alpha')^2] \; . \end{aligned} \tag{31}$$

Thus, by comparing the left-hand side of Eq. (29) with the right-hand side of Eq. (30), the following relations result:

$$E_d' \equiv E_d' + \Delta E_d' \; , \quad W \equiv \frac{\gamma_d}{\alpha'} \equiv \frac{2 \operatorname{Im}\alpha \operatorname{Re}\alpha'}{(\operatorname{Re}\alpha')^2 + (\operatorname{Im}\alpha')^2} \; . \tag{32}$$

These are standard results (see, for example, Ref. 18, p. 9); and for the relations in Eq. (32) to be consistent, we must set $\Delta E_d' = 0$, so that

$$\operatorname{Im}\alpha' = 0 \; , \quad \text{i.e.,} \quad \operatorname{Im}\alpha = \text{const.} \tag{33}$$

Thus, we find that $\gamma_d = 2(\operatorname{Im}\alpha)$ is a constant (independent of energy), and

$$W = \gamma_d (\operatorname{Re}\alpha')^{-1} \equiv \gamma_d \left(\frac{dE}{dl}\right)_{l=2} \; . \tag{34}$$

This is the main result of the Regge-pole theory in this paper. It goes beyond the existing formulations of the resonance model in so far as it ex-

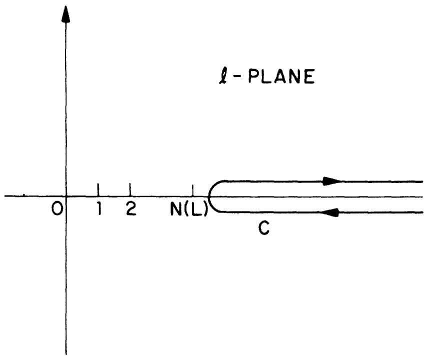

FIG. 2. Contour (C) in l plane used in Eq. (35) (after Squires, Ref. 19, p. 5).

hibits for the first time, the dependence of W on the variation of E with the angular-momentum quantum number l, in the neighborhood of $l=2$.

We may now delve more deeply into the foundations of Eq. (27), since this is of interest by itself. We apply the so-called Watson-Sommerfeld transformation[19] to the final form of the KKR pseudopotential form factor in Eq. (24):

$$\tilde{V}^{\mathrm{KKR}}(\vec{k},\vec{k}')=\frac{4\pi}{\Omega_0}\sum_{l=0}^{N(L)}(2l+1)\,T_l\,P_l(\cos\theta_{\vec{k}\vec{k}'})+\frac{2\pi i}{\Omega_0}\int_C(2\alpha+1)\,T_\alpha\,\frac{P_\alpha(\cos\theta_{\vec{k}\vec{k}'})}{\sin\pi\alpha}\,d\alpha\ , \tag{35}$$

where C is the contour in the complex l plane shown in Fig. 2, and $N(L)$ is the largest positive integer less than or equal to some fixed angular-momentum quantum number L. The integral in this equation is equal to the sum of the residues of the poles which arise from the zeroes of $\sin\pi\alpha$ at positive integers greater than or equal to L.

Now, in simple metals, T_α does not have any pole in the complex l plane. In this case, the integral in Eq. (35) reproduces the remaining terms of the partial-wave expansion. But in transition metals, there is an $l=2$ resonance and there will be a contribution from such a resonance to the total pseudopotential form factor. That is, Eq. (35) takes the form

$$\tilde{V}^{\mathrm{KKR}}(\vec{k},\vec{k}')=\frac{4\pi}{\Omega_0}\sum_{l\neq 2}(2l+1)\,T_l P_l(\cos\theta_{\vec{k}\vec{k}'})-(8\pi^2/\Omega_0)(2\alpha+1)\,t_d\,\frac{P_\alpha(\cos\theta_{\vec{k}\vec{k}'})}{\sin\pi\alpha}\bigg|_{l=2}\ , \tag{36}$$

where t_d is the residue of T_α at the pole of the $l=2$ partial-wave amplitude. Thus, by comparing Eqs. (26) and (36), we obtain the identity

$$2\pi\gamma_d/\sin\pi\alpha\equiv\tfrac{1}{2}W/(E_d'-E+\tfrac{1}{2}iW)\ , \tag{37}$$

where γ_d is defined in terms of the residue t_d by the relation

$$t_d=\kappa^{-1}\gamma_d j_2(kR)\,j_2(k'R)/[\,j_2(\kappa R)]^2\ . \tag{38}$$

Upon making the following approximation, which is valid near the resonance energy $E=E_d'$:

$$\csc\pi\alpha\approx\pi^{-1}[(E_d'-E)\,\alpha'+i\,\mathrm{Im}\alpha\,]^{-1}\ , \tag{39}$$

Eq. (37) reduces to Eq. (29), as desired.

It should be stressed that the result in Eq. (34) is model independent because it has been derived from a T-matrix form factor, rather than an ordinary pseudopotential form factor. This means that it can be interpreted quantitatively in the context of any valid transition-metal pseudopotential form factor, that is any pseudopotential form factor exhibiting the T-matrix structure for the $l=2$ partial-wave amplitude for scattering.

IV. INTERPRETATION IN THE TRANSITION-MODEL-POTENTIAL METHOD

The result of the Regge-pole theory described in Sec. III will now be interpreted in the framework of the transition-metal-model-potential (TMMP) method discussed in the first two papers[1,2] of this series. As in Sec. II above, the TMMP form factor (Ref. 1, Appendix A) for one-electron energy bands (Ref. 2, Sec. I) is expected to be different from the form factor for scattering at arbitrary energies in the crystal, and the difference is exhibited by the TMMP parameter, $A_2(E)$, for the $l=2$ angular momentum state [see Fig. 1(b)].

Before we write down the forms of $A_2(E)$, a few words about notation are in order. In the TMMP method, the analog of E_d' is denoted by $\mathcal{E}_{nd}$ ($n=3$, 4, 5 for the respective $3d$, $4d$, and $5d$ series of transition metals), and the analog of W will be denoted by W_{nd}: it is not necessary to assume that $E_d'\equiv\mathcal{E}_{nd}$ and $W\equiv W_{nd}$, but we hope to provide sufficient reasons below to justify their identification. The shifted energy $\mathcal{E}_{nd}$ has been defined (for arbitrary angular momentum state) in Eq. (6) of Ref. 1 in terms of the true spectroscopic term values E_{nd} via the generalized (empirical) quantum defect law:

$$\mathcal{E}_{nl}\equiv-z^2/(n-\delta_{nl})^2=E_{nl}-\Delta_{nl}\ , \tag{40}$$

where δ_{nl}, Δ_{nl} are fixed (independent of z) for fixed radial and angular-momentum quantum numbers (n, l) and z is the chemical valence of the pertinent transition-metal ion in an isoelectronic sequence, such as

$$\mathrm{Sc}^{3+},\ \mathrm{Ti}^{4+},\ \mathrm{V}^{5+},\ \mathrm{Cr}^{6+},\ \ldots\ , \tag{41}$$

i.e., elements characterized by the same inert-gas core configuration along a row of the Periodic Table. The significance of Eq. (40) is exhibited in Fig. 3(a) for $n=4$ ($l=0$, 1, 2, 3) levels of the $3d$ transition series: it would have been more per-

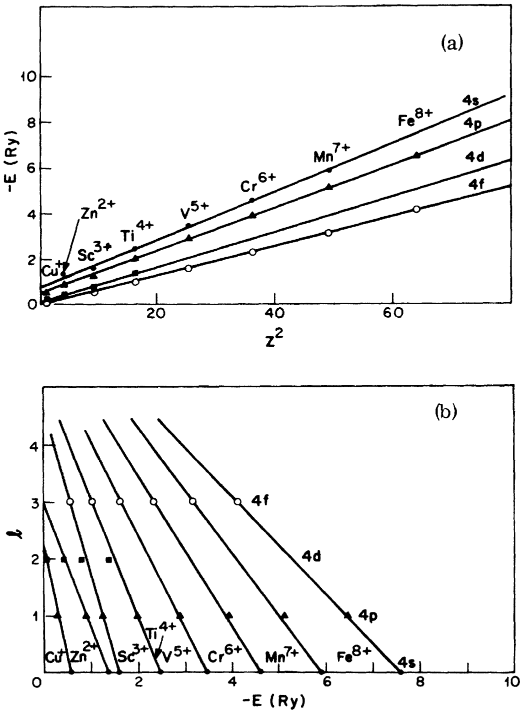

FIG. 3. (a) Spectroscopic term values E_{nl} as function of the square (z^2) of the chemical valence for group-B elements of the $3d$ series in the Periodic Table, illustrating the generalized quantum defect law in Eq. (40) (for more details, see Ref. 1). (b) The same term values E_{nl} plotted as functions of the angular momentum l defining the spectroscopic Regge trajectories. [Note that the Rydberg series $E_{nl} \equiv -z^2/n^2$ gives for $n=4$, $E_{4s}=E_{4p}=E_{4d}=E_{4f}$ and therefore leads to trajectories parallel to the l axis; the deviation of the actual trajectories from being parallel to the l axis provides, therefore, a measure of intra-atomic electron-electron interaction effects).

tinent to consider the term values for $n=3$ but, unfortunately, these are not available,[9] except for $n=3$, $l=2$ which has been displayed in Fig. 4 of Ref. 1. Furthermore, the spectroscopic Regge trajectories, l vs E_{nl} are shown in Fig. 3(b) for the same $n=4$ ($l=0$, 1, 2, 3) of Fig. 3(a): the trajectories are linear for fixed n.

With these preliminaries, the resonance model is given in the TMMP method by the relations

$$\begin{aligned} A_2(E) &\propto \tfrac{1}{2} W_{nd}(\mathcal{E}_{nd}-E)^{-1} \quad \text{for energy bands} \\ &\propto \tfrac{1}{2} W_{nd}(\mathcal{E}_{nd}-E+\tfrac{1}{2} i W_{nd})^{-1} \quad \text{for scattering ,} \end{aligned} \tag{42}$$

where $\mathcal{E}_{nd}$ is determined semiempirically [as in Fig. 1(b)] from the singularity in $A_2(E)$ vs E; and W_{nd} is given [as in Eq. (34)] by

$$W_{nd} = \gamma_d \left(\frac{dE_{nl}}{dl} \right)_{l=2} , \tag{43}$$

which may be looked up from the slope of l vs E_{nl} for the pertinent term values.

In the absence of spectroscopic data, Eqs. (40) and (43) may be used to make qualitative prediction about the variation of W_{nd} with chemical valence (z) in an isoelectronic sequence, such as the sequence in Eq. (41), as follows. We substitute E_{nl} from Eq. (40) into Eq. (43) to find

$$W_{nd} = \gamma_d(\mu_{nd} z^2 + \gamma_{nd}) , \tag{44}$$

where

$$\mu_{nd} = \frac{d}{dl} \frac{-1}{(n-\delta_{nl})^2} \bigg|_{l=2} , \quad \nu_{nd} = \frac{d\Delta_{nl}}{dl} \bigg|_{l=2} . \tag{45}$$

Since γ_d in Eq. (44) is independent of energy, (and hence independent of z), it follows that W_{nd} vs z^2 is linear in an isoelectronic sequence (see Fig. 4).

Now, because W_{nd} vs z^2 as well as E_{nd} vs z^2 are linear, it follows that in Eq. (42), for values of E close to the spectroscopic term values

$$(\mathcal{E}_{nd}-E)/\tfrac{1}{2} W_{nd} = \cot\eta_2'(E) \tag{46}$$

is practically independent of z in an isoelectronic sequence. Therefore, the d-band width (Δ), determined as in Eq. (18) by the relation

$$\Delta \equiv \mathcal{E}_{nd} - E_0 = \tfrac{1}{2} W_{nd} \cot\eta_2'(E_0) , \tag{47}$$

derives its z dependence from that of W_{nd} and accordingly Δ vs z^2 will be linear in an isoelectronic sequence. This prediction is seen in Fig. 4 to be in agreement with the results derived from the APW and renormalized atom methods.[16] For this reason, we are encouraged to say that the TMMP method agrees, or can be made to agree, with the APW method in detail, both with regard to the posi-

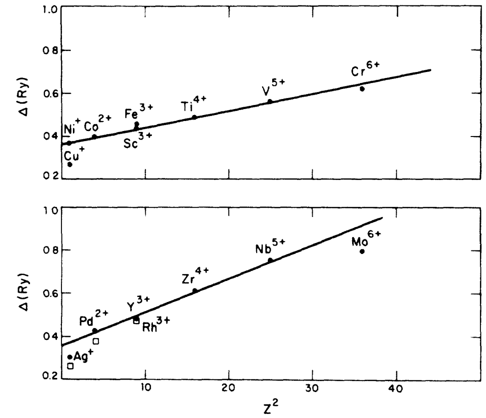

FIG. 4. Straight lines represent the relation Δ vs z^2 of Eqs. (44) and (46), between the d-band width (Δ) and the chemical valence (z); the points are the results of APW and/or renormalized atom methods given in Fig. 8 of Ref. 16; the squares are results of recent photoemission studies obtained by Smith and Traum (Ref. 17).

tion of the d band [cf. Figs. 1(a) and 1(b)] and with regard to the d-band width (Fig. 4). This agreement will be put on a more quantitative basis in Paper IV.

It is also of interest to find an expression for the *hybridization gap* γ, which is defined in such a way that Eq. (14) reduces to

$$(E - k^2)(E - E'_d) = \gamma^2 , \tag{48}$$

i.e., in the KKR method

$$\gamma = (10\pi/\Omega_0 \kappa_d)^{1/2} W^{1/2} . \tag{49}$$

Similarly, in the TMMP method, γ^2 is the coefficent of $(\mathcal{E}_{nd} - E)^{-1}$ in the matrix element $\langle \vec{k}' | A_2 \times \Theta(R_M - r) P_2 | \vec{k} \rangle$, of the screened TMMP, P_2 being the projection operator that picks out the $l = 2$ component of the plane wave $|\vec{k}\rangle$, and $\Theta(x) = 1$ (for $x \geq 0$) but zero otherwise. Thus, proceeding as in Appendix A of Ref. 1, we find

$$\gamma^2 \propto W_{nd} \left(20\pi \int_0^{R_m} j_2(kr) j_2(k'r) r^2 \, dr / \Omega_0 \epsilon(|\vec{k} - \vec{k}'|) \right) \times \tfrac{1}{2}(3\cos^2\theta_{\vec{k}\vec{k}'} - 1) , \tag{50}$$

where $\epsilon(|\vec{k} - \vec{k}'|)$ is the dielectric function of the free electron gas. This leads to $\gamma \propto W_{nd}^{1/2}$ as in Eq. (49). In transition metals, 2γ and Δ turn out to be numerically the same order of magnitude, but they have different functional dependence on W_{nd}.

V. COMPARISON OF NUMERICAL RESULTS WITH EXPERIMENT

In this section we wish to compare the numerical results shown in Fig. 4 with the only available experimental "test" of the resonance model provided by recent photoemission data.[17] With the assignment of chemical valence given in Fig. 4, which agrees with the assignment proposed in Ref. 1 for all but Ni [taken to be Ni^{2+} in Ref. 1 but Ni^+ here], the linear relation Δ vs z^2 is quite well satisfied for transition mentals of the respective $3d$ and $4d$ series, and there is fair agreement with the results deduced from photoemission data by Smith and Traum.[17]

In assessing the significance of these results we must first caution that our predictions strictly apply to isoelectronic sequences, i.e., Sc^{3+}, Ti^{4+}, V^{5+}, and Cr^{6+} but not Ni^+, Co^{2+}, Fe^{3+}, and Cu^+ in the $3d$ series; and Y^{3+}, Zr^{4+}, Nb^{5+}, and Mo^{6+} but not Pd^{2+}, Rh^{3+}, and Ag^+, in the $4d$ series. Thus, agreement with the photoemission data on Cu, Ag, Pd, and Rh is significant only in so far as the present theory serves as a basis for correlating the results in terms of a fundamental parameter, such as the chemical valence. Secondly, the photoemission data have been interpreted in the framework of one-electron energy bands derived from the interpolated scheme of Hodges, Ehrenreich, and Lang[20]; it is not clear what role many-electron effects may play in determining the position of the peaks in the raw data.

Another aspect of the comparison with the photoemission data is the structure of the higher (sp) *conduction bands* deduced by fitting the photoemission spectrum with the one-electron energy bands via the interpolation scheme, as recently discussed by Smith and Mattheiss[21] and Smith.[22] This will be considered in Paper V of this series, where it will be shown that the TMMP form factor captures the essence of the interpolation scheme by providing an interpretation of the empirical pseudopotential matrix elements that characterize the conduction bands in the interpolation scheme.

VI. SUMMARY AND CONCLUSIONS

In this paper, we have reformulated the resonance model of s-d hybridization in transition metals in terms of the analytical properties of transition-metal pseudo- or model-potential form factors, so as to make the model consistent and useful not only for interpreting the results of one-electron energy band calculations, but also for studying various scattering processes in the crystal. This has been achieved by making use of the Regge-pole theory in solid state physics; and as a result, we have been able to relate the two parameters of the resonance model to each other and hence provide a basis for obtaining the parameters from the systematics of the atomic spectroscoptic data. New insight has been gained into the systematic variation of the d-bandwidth with the chemical valence along the $3d$, $4d$, and $5d$ transition series; and more light has been shed on the connection between the practical aspects of the APW method and those of the transition-metal model potential method.

Although we have not touched upon a number of important problems, notably those associated with the magnetic properties of the transition metals, the results derived thus far from the transition-metal model potential program encourage us to draw a few firm conclusions. First, the transition-metal model potential method has shown signs of succeeding in a number of areas—phonon spectra, electron-phonon interaction, and the resonance model of s-d hybridization—where other available theories have had conceptual and computational difficulties. Second, the method has uncovered a number of empirical results—atomic spectroscopic data, systematic variation of Debye (or better, jellium) temperature, superconducting transition temperature, and the d bandwidth with the chemical valence—which future models have to incorporate or explain. Finally, it has affirmed our basic belief that by judicious blending of rudimentary facts of atomic physics and new tools of high-energy physics, (such as the atomic spectra and the Regge pole theory respectively), something useful could be learned about the electronic structure and properties of solids.

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[1] A. O. E. Animalu, Phys. Rev.d B 8, 3542 (1973).

[2] A. O. E. Animalu, Phys. Rev. B 8, 3555 (1973).

[3] J. M. Ziman, Proc. Phys. Soc. Lond. 86, 337 (1965); G. J. Morgan, *ibid.* 89, 365 (1966).

[4] V. Heine, Phys. Rev. 153, 673 (1967).

[5] J. Hubbard, Proc. Phys. Soc. Lond. 92, 921 (1967); R. Jacobs, J. Phys. C 1, 1296, 1307 (1968).

[6] See, for example, G. Baym, *Lectures on Quantum Mechanics* (Benjamin, New York, 1969), pp. 197–233.

[7] T. Regge, Nuovo Cimento 14, 951 (1959); 18, 947 (1960).

[8] For an elementary review of the Regge-pole theory in nonrelativistic potential scattering theory, see R. Kronenfeld, Am. J. Phys. 39, 1056 (1971); and also Ref. 6, pp. 219–223.

[9] C. E. Moore, *Atomic Energy Levels*, Natl. Bur. Stds. (U.S. GPO, Washington, D.C., 1949), Vols. I, II, and III.

[10] J. Korringa, Physica (Utr.) 13, 392 (1947); W. Kohn and N. Rostoker, Phys. Rev. 94, 1111 (1954).

[11] T. L. Loucks, *Augmented Plane Wave Method* (Benjamin, New York, 1967).

[12] W. A. Harrison, *Pseudopotentials in the Theory of Metals* (Benjamin, New York, 1966); W. A. Harrison, Phys. Rev. 181, 1036 (1969); J. A. Moriarty, Phys. Rev. B 6, 1239 (1972).

[13] M. L. Cohen and V. Heine, Solid State Phys. 24, 37 (1970).

[14] M. J. G. Lee and V. Heine, Phys. Rev. B 5, 3839 (1972).

[15] L. D. Landau and E. M. Lifshitz, *Quantum Mechanics* (Pergamon, London, 1958), pp. 441-3.

[16] L. Hodges, R. E. Watson, and H. Ehrenreich, Phys. Rev. B 5, 3953 (1972).

[17] N. V. Smith and M. M. Traum, Phys. Rev. Lett. 29, 1243 (1972); D. E. Eastman and W. D. Grobman, Phys. Rev. Lett. 30, 177 (1973).

[18] R. G. Newton, *The Complex j-Plane* (Benjamin, New York, 1964).

[19] E. J. Squires, *Complex Angular Momentum and Particle Physics* (Benjamin, New York, 1964).

[20] L. Hodges, H. Ehrenreich, and N. D. Lang, Phys. Rev. 152, 505 (1966); F. M. Mueller, Phys. Rev. 153, 659 (1967).

[21] N. V. Smith and L. F. Mattheiss, Phys. Rev. B (to be published).

[22] N. V. Smith, Phys. Rev. B (to be published).