sum rule becomes

$$Z=-\frac{2}{\hbar(2\pi)^3}\int_{E_F}\frac{dS\,\mathrm{Re}t_{\mathbf{kk}}}{v_0(\mathbf{k})}\,. \qquad \text{(A11)}$$

We note from (A7) that the average value of $\mathrm{Re}t_{\mathbf{kk}}$ depends on only Z, the valence charge difference between the impurity and the host, and not on the details of the potential. When $Z=0$, $t_{\mathbf{kk}}$ can be small and one expects that it can be calculated from perturbation theory. However, for $Z\neq 0$ in the noble metals, $t_{\mathbf{kk}}$ cannot be small and, as we argued in Sec. II, cannot be calculated from perturbation theory. Nevertheless, the total scattering by the t matrix could still be small, i.e., $t_{\mathbf{kk}'}$, could be small for most $\mathbf{k}'$ as discussed in Sec. II. The Friedel sum rule fixes the average value of $t_{\mathbf{kk}}$ at an appreciable value for $Z\neq 0$ and $t_{\mathbf{kk}'}$ then must go rapidly to small values as $\mathbf{k}'$ moves away from $\mathbf{k}$. Thus t produces scattering which is strongly peaked in the forward direction.

PHYSICAL REVIEW VOLUME 188, NUMBER 3 15 DECEMBER 1969

Alternative Transition-Metal Pseudopotential*

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(Received 16 June 1969)

We consider the pseudopotential interaction between the s-like electrons in metals that also contain d electrons, using Hubbard's hybrid representation of the Korringa-Kohn-Rostoker (KKR) band-structure method, in a manner similar to that recently employed by the author in discussing the total energy of d-band metals. The interaction is formulated as a sum of two parts: (1) a direct interaction between orthogonalized plane waves (OPW's), which is similar to the "transition-metal pseudopotential" recently defined by Harrison from a modified OPW viewpoint, and (2) an indirect interaction via the d electrons, similar to Harrison's "hybridizing terms." We then combine these two parts and arrive at the KKR-Ziman form of the pseudopotential as the resultant effective interaction. The author's previous result for the total energy of an alkaline earth or noble metal is reinterpreted as the consequence of using the KKR-Ziman pseudopotential with a d-scattering resonance.

I. INTRODUCTION

THIS paper is concerned with calculating the effective pseudopotential interaction between the s-like electrons in transition and near-transition metals, where the presence of the d bands in the electronic structure must be taken into account. Harrison[1] has treated this problem by considering the band structure from a modified orthogonalized-plane-wave (OPW) point of view, where the basis set of functions contains both OPW'S and atomiclike d functions[2]; he has in this way derived an effective pseudopotential interaction between the OPW states. Here we begin instead with the band structure represented by Hubbard and Dalton's[3,4] hybrid secular equation, which is based on a transformation of the Korringa-Kohn-Rostoker (KKR) method, and we formulate the pseudopotential interaction in these terms; the procedure employed is a generalization of that used by the author in deriving an expression for the total energy of the alkaline earth and noble metals.[5]

We obtain the pseudopotential interaction as the sum of two parts: The first part represents a direct interaction between OPW's and is similar to Harrison's[1] transition-metal pseudopotential; the second part represents an indirect interaction via the d electrons, similar to the hybridizing terms of Harrison's treatment. These two parts are then combined, and it is shown that the resultant effective pseudopotential reduces to the KKR-Ziman[6] (KKRZ) pseudopotential containing the full phase shift, including the d-scattering resonance, which is the result to be expected. Our previous expression for the total energy of an alkaline earth or noble metal can then be reinterpreted as the consequence of using the KKRZ form of the pseudopotential with a d-scattering resonance.

II. EFFECTIVE INTERACTION BETWEEN OPW'S

In the KKR method of band-structure calculation the muffin-tin approximation is used; the one-electron crystalline potential is approximated by a sum of non-

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* Supported in part by the U. S. Army Research Office (Durham), under Contract No. DA-HCO4-69-C-0007.

[1] W. A. Harrison, Phys. Rev. 181, 1036 (1969).

[2] See, e.g., R. A. Deegan and W. D. Twose, Phys. Rev. 164, 993 (1967).

[3] J. Hubbard, Proc. Phys. Soc. (London) 92, 921 (1967).

[4] J. Hubbard and N. W. Dalton, J. Phys. C1, 1637 (1968).

[5] R. A. Deegan Phys. Rev. 186, 619 (1969).

[6] J. M. Ziman, Proc. Phys. Soc. (London) 86, 337 (1965).

overlapping spherical potentials centered on each lattice site. The potential then enters the solution of the Schrödinger equation for the crystal only through the phase shifts of this spherical potential. In a transition metal the $l=2$ phase shift has the following resonant form[6] (following Refs. 3 and 4, we use the symbol λ for the orbital angular momentum of the resonant state, which for a transition metal is $\lambda=2$):

$$t_\lambda(\epsilon)\equiv\tan\eta_\lambda(\epsilon)=\Gamma/(\epsilon_0-\epsilon)+t_\lambda{}^s(\epsilon)\,, \tag{2.1}$$

where η_l denotes the l phase shift, Γ and ϵ_0 are the width and position of the λ scattering resonance, and $t_\lambda{}^s$ is a smooth residual phase shift, which is small. (The quantity ϵ_0 determines the position of the d bands in the electronic structure of the transition metals.)

Hubbard and Dalton[3,4] have shown that, for such a resonance in the phase shift, the KKR equations determining the eigenfunctions and eigenvalues can be approximately transformed to the following hybrid form [see HD (30) and (31); we use the symbol HD to denote equation numbers in Ref. 4]:

$$\begin{pmatrix}\mathbf{C} & \mathbf{H}^\dagger\\ \mathbf{H} & \mathbf{D}\end{pmatrix}\begin{pmatrix}\mathbf{b}\\ \mathbf{a}\end{pmatrix}=0\,. \tag{2.2}$$

In this equation, $\mathbf{b}$ is a column vector with components $b_\mathbf{K}$, which are the coefficients of OPW's of wave vector $\mathbf{k}+\mathbf{K}$, with $\mathbf{K}$ denoting the reciprocal lattice vectors of the crystal; $\mathbf{a}$ is a column vector with components a_m, which are the coefficients of localized d functions having magnetic quantum number m; and $\mathbf{C}$, $\mathbf{D}$, and $\mathbf{H}$ are matrices representing, respectively, the conduction [or nearly-free-electron (NFE)] bands, the d bands, and the hybridization between them. The matrix elements can be written as [HD (30)–(33), or see Eqs. (2.5)–(2.7) of Ref. 5]

$$C_{\mathbf{KK}'}=(|\mathbf{k}+\mathbf{K}|^2-\epsilon)\delta_{\mathbf{KK}'}+v_{\mathbf{KK}'}(\mathbf{k},\epsilon)\,, \tag{2.3}$$

$$D_{mm'}=(\epsilon_0-\epsilon)\delta_{mm'}+O(\Gamma)\,, \tag{2.4}$$

$$H_{m\mathbf{K}}=\Gamma^{1/2}\hat{h}_m(\mathbf{k}+\mathbf{K})+O(\Gamma^{1/2}v)\,, \tag{2.5}$$

where $\epsilon(\mathbf{k})$ are the desired energy bands, and the NFE pseudopotential function $v_{\mathbf{KK}'}$ and the hybridization function $\hat{h}_m$ are defined in Ref. 4. Note from (2.5) that the resonance width Γ controls the strength of the hybridization; here we will retain only lowest-order terms in Γ when calculating the effect of the d bands on the plane-wave interaction.

To obtain the effect of the d bands on the NFE bands, we follow a procedure employed by Heine,[7] and multiply (2.2) on the left-hand side by the matrix

$$\begin{pmatrix}\mathbf{I} & -\mathbf{H}^\dagger\mathbf{D}^{-1}\\ -\mathbf{H}\mathbf{C}^{-1} & \mathbf{I}\end{pmatrix}, \tag{2.6}$$

where $\mathbf{I}$ denotes unit matrices, giving

$$\begin{pmatrix}\mathbf{C}-\mathbf{H}^\dagger\mathbf{D}^{-1}\mathbf{H} & 0\\ 0 & \mathbf{D}-\mathbf{H}\mathbf{C}^{-1}\mathbf{H}^\dagger\end{pmatrix}\begin{pmatrix}\mathbf{b}\\ \mathbf{a}\end{pmatrix}=0\,. \tag{2.7}$$

The equation for the coefficients $b_\mathbf{K}$ is then

$$(\mathbf{C}')(\mathbf{b})=0\,, \tag{2.8}$$

where we have defined

$$\mathbf{C}'\equiv\mathbf{C}-\mathbf{H}^\dagger\mathbf{D}^{-1}\mathbf{H}\,. \tag{2.9}$$

From (2.4) and (2.5), the matrix $\mathbf{H}^\dagger\mathbf{D}^{-1}\mathbf{H}$ has elements

$$\Gamma\sum_m\frac{\hat{h}_m{}^*(\mathbf{k}+\mathbf{K})\hat{h}_m(\mathbf{k}+\mathbf{K}')}{\epsilon_0-\epsilon}\,, \tag{2.10}$$

where the last terms on the right-hand sides of (2.4) and (2.5) have been ignored since they contribute to orders Γ^2 and Γv^2, respectively. The matrix elements of $\mathbf{C}'$ in (2.8) are then

$$C_{\mathbf{KK}'}{}'=(|\mathbf{k}+\mathbf{K}|^2-\epsilon)\delta_{\mathbf{KK}'}+v_{\mathbf{KK}'}{}'(\mathbf{k},\epsilon)\,, \tag{2.11}$$

where we have defined

$$v_{\mathbf{KK}'}{}'\equiv v_{\mathbf{KK}'}-\Gamma\sum_m\frac{\hat{h}_m{}^*(\mathbf{k}+\mathbf{K})\hat{h}_m(\mathbf{k}+\mathbf{K}')}{\epsilon_0-\epsilon}\,. \tag{2.12}$$

Equation (2.12) defines an effective pseudopotential v'. The first term on the right-hand side represents a direct interaction between the OPW's of wave vector $(\mathbf{k}+\mathbf{K})$ and $(\mathbf{k}+\mathbf{K}')$, and appears to correspond to the transition-metal pseudopotential W of Harrison's[1] treatment; the last term on the right-hand side of (2.12) represents an indirect interaction of the plane waves via the d electrons, similar to the hybridizing terms of Ref. 1.

III. SIMPLIFICATION OF PSEUDOPOTENTIAL

In Sec. II we formulated the effective pseudopotential interaction in terms of the hybrid KKR scheme. We now use the explicit form of the functions $v_{\mathbf{KK}'}$ and $\hat{h}_m$ of that scheme to combine the two terms on the right-hand side of (2.12); it is shown that $v_{\mathbf{KK}'}{}'$ then reduces simply to the KKRZ pseudopotential, containing the full d phase shift, including the resonance.

The hybridization function $\hat{h}_m$ is given by [HD (19)]

$$\hat{h}_m(\mathbf{k}+\mathbf{K})=f^{1/2}(\epsilon)F_{\lambda m}(\mathbf{k}+\mathbf{K},\,\epsilon)\,, \tag{3.1}$$

with the definitions [HD (4) and (7)]:

$$f(\epsilon)\equiv(\epsilon/\epsilon_0)^{\lambda+1/2}e^{(\epsilon_0-\epsilon)/\beta} \tag{3.2}$$

and

$$F_{lm}(\mathbf{k}+\mathbf{K},\,\epsilon)\equiv\frac{4\pi}{\tau^{1/2}}\frac{|\mathbf{k}+\mathbf{K}|^l}{\kappa^{l+1/2}}Y_{lm}{}^*(\mathbf{k}+\mathbf{K})\times\exp\frac{\epsilon-|\mathbf{k}+\mathbf{K}|^2}{2\beta}\,, \tag{3.3}$$

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

where τ is the volume per atom, $\kappa=\epsilon^{1/2}$, and β is the Ewald-like splitting parameter of the hybrid scheme.[3] Then the last term in (2.12) becomes

$$\Gamma\sum_m \frac{\hat{h}_m^*(\mathbf{k}+\mathbf{K})\hat{h}_m(\mathbf{k}+\mathbf{K}')}{\epsilon_0-\epsilon}=\frac{\Gamma f(\epsilon)}{\epsilon_0-\epsilon} \times\sum_m F_{\lambda m}^*(\mathbf{k}+\mathbf{K},\,\epsilon)F_{\lambda m}(\mathbf{k}+\mathbf{K}',\,\epsilon). \quad (3.4)$$

The pseudopotential $v_{\mathbf{KK}'}$ of (2.12) can be written as [see HD (21) and (12), and Eqs. (3.5) and (3.6) of Ref. 5]

$$v_{\mathbf{KK}'}=-\sum_{lm}\left[t_l+\delta_{l\lambda}(t_\lambda^s+t_\lambda''-t_\lambda)\right] \times F_{lm}^*(\mathbf{k}+\mathbf{K},\,\epsilon)F_{lm}(\mathbf{k}+\mathbf{K}',\,\epsilon), \quad (3.5)$$

where

$$t_\lambda''(\epsilon)=[\Gamma/(\epsilon_0-\epsilon)][1-f(\epsilon)] \quad (3.6)$$

and $t_l\equiv\tan\eta_l$. [Here, as in Ref. 5, we have replaced the denominator of HD (12) by unity, to lowest order in the phase shifts. Also, we have retained the energy dependence of the pseudopotential HD (17), rather than evaluating it at $\epsilon=k^2$, as in HD (21).] From (3.4)–(3.6), and (2.1), Eq. (2.12) becomes

$$v_{\mathbf{KK}'}{}'=-\sum_{lm} t_l F_{lm}^*(\mathbf{k}+\mathbf{K},\,\epsilon)F_{lm}(\mathbf{k}+\mathbf{K}',\,\epsilon), \quad (3.7)$$

which, for $l=\lambda$, contains the full phase shift t_λ of (2.1).

Substituting from (3.3), this becomes

$$v_{\mathbf{KK}'}{}'=-\frac{4\pi}{\tau}\sum_l \frac{(2l+1)}{\kappa^{2l+1}}t_l|\mathbf{k}+\mathbf{K}|^l|\mathbf{k}+\mathbf{K}'|^l \times\exp\left(\frac{2\epsilon-|\mathbf{k}+\mathbf{K}|^2-|\mathbf{k}+\mathbf{K}'|^2}{2\beta}\right)P_l\cos(\theta_{\mathbf{KK}'}), \quad (3.8)$$

where $\theta_{\mathbf{KK}'}$ denotes the angle between the vectors $(\mathbf{k}+\mathbf{K})$ and $(\mathbf{k}+\mathbf{K}')$. This can be simplified by noting that, to lowest order, $v'_{\mathbf{KK}'}$ will be physically significant only for energies $\epsilon=\kappa^2\simeq|\mathbf{k}+\mathbf{K}|^2\simeq|\mathbf{k}+\mathbf{K}'|^2$; making this approximation, we obtain

$$v_{\mathbf{KK}'}{}'=-\frac{4\pi}{\kappa\tau}\sum_l (2l+1)t_lP_l(\cos\theta_{\mathbf{KK}'}). \quad (3.9)$$

This is just the KKRZ form of the pseudopotential [Eq. (52) of Ref. 6, in the limit $(r,\,r'\rightarrow 0)$], where we have made the approximation $\kappa^2\simeq|\mathbf{k}+\mathbf{K}|^2\simeq|\mathbf{k}+\mathbf{K}'|^2$.

Finally, we note that the lowest-order effect of the λ resonance on the first conduction band is, from (3.9),

$$v_{00}'(\text{resonance})=-\frac{4\pi(2\lambda+1)}{\kappa\tau}\frac{\Gamma}{\epsilon_0-\epsilon}. \quad (3.10)$$

Replacing ϵ by k^2, this becomes the term $\Gamma(\Delta\epsilon)_\lambda$ [see Eq. (3.15) of Ref. 5] which was integrated over the Fermi sphere in Ref. 5 to give the expression for the total energy of an alkaline earth or noble metal; the remaining terms of (3.9) give the NFE pseudopotential $v_{\mathbf{KK}'}{}^s$ introduced in Ref. 5.

IV. SUMMARY AND DISCUSSION

This paper contains a formulation from the hybrid KKR point of view of the effective pseudopotential interaction in the presence of *d* electrons. We have obtained this interaction as a sum of direct and indirect terms, similar to Harrison's[1] formulation of this problem from a modified OPW viewpoint; in combining these terms we have essentially unfolded the hybrid scheme into the KKR plane-wave representation of Ziman.[6] This throws new light on our previous results for the total energy of near-transition metals, and also emphasizes the usefulness of the KKRZ formulation for these materials. Finally, we note that, in dealing with transition metals, a hybrid-KKR treatment of the type considered here may be the most suitable method for explicitly taking into account the partially filled *d* bands.