For such a class of potentials, the T-matrix equation reads

$$T(\vec{k}',\vec{k})=\sum_\Gamma A_\Gamma v_\Gamma(\vec{k}')v_\Gamma^*(\vec{k})+\sum_\Gamma A_\Gamma v_\Gamma(\vec{k}')\times\int\frac{d\vec{t}}{(2\pi)^3}\,\frac{v_\Gamma^*(\vec{t})T(\vec{t},\vec{k})}{E_{\vec{k}}-E_{\vec{t}}+i\epsilon}\,. \tag{B4}$$

Introduce the auxiliary notation

$$x_\Gamma(\vec{k})=\int\frac{d\vec{t}}{(2\pi)^3}\,\frac{v_\Gamma^*(\vec{t})T(\vec{t},\vec{k})}{E_{\vec{k}}-E_{\vec{t}}+i\epsilon}\,, \tag{B5a}$$

which gives for (B4)

$$T(\vec{k}',\vec{k})=\sum_\Gamma A_\Gamma v_\Gamma(\vec{k}')v_\Gamma^*(\vec{k})+\sum_\Gamma A_\Gamma v_\Gamma(\vec{k}')x_\Gamma(\vec{k})\,. \tag{B5b}$$

From (B5b) it is possible to derive a system of linear equations determining the $x_\Gamma(\vec{k})$. Multiplying (B5b) by $v_{\Gamma_1}^*(\vec{k}')/(E_{\vec{k}}-E_{\vec{k}'}+i\epsilon)$ and summing over $\vec{k}'$ one gets

$$\int\frac{d\vec{t}'}{(2\pi)^3}\,\frac{v_{\Gamma_1}^*(\vec{k}')T(\vec{k}',\vec{k})}{E_{\vec{k}}-E_{\vec{k}'}+i\epsilon}=\sum_\Gamma A_\Gamma v_\Gamma^*(\vec{k})\int\frac{d\vec{k}'}{(2\pi)^3}\,\frac{v_{\Gamma_1}^*(\vec{k}')v_\Gamma(\vec{k}')}{E_{\vec{k}}-E_{\vec{k}'}+i\epsilon}+\sum_\Gamma A_\Gamma x_\Gamma(\vec{k})\int\frac{v_{\Gamma_1}^*(\vec{k}')v_\Gamma(\vec{k}')}{E_{\vec{k}}-E_{\vec{k}'}+i\epsilon}\,\frac{d\vec{k}'}{(2\pi)^3}\,, \tag{B6}$$

which can be written as

$$x_{\Gamma_1}(\vec{k})=B_{\Gamma_1}(\vec{k})+\sum A_{\Gamma\Gamma_1}(\vec{k})x_\Gamma(\vec{k})\,, \tag{B7a}$$

where

$$A_{\Gamma\Gamma_1}(\vec{k})=A_\Gamma\int\frac{d\vec{k}'}{(2\pi)^3}\,\frac{v_{\Gamma_1}^*(\vec{k}')v_\Gamma(\vec{k}')}{E_{\vec{k}}-E_{\vec{k}'}+i\epsilon}\,, \tag{B7b}$$

$$B_{\Gamma_1}(\vec{k})=\sum_\Gamma v_\Gamma^*(\vec{k})A_{\Gamma\Gamma_1}(\vec{k})\,. \tag{B7c}$$

Equations (B7) and (B5b) provide the *exact* solutions for the T matrix.

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Pseudopotential Approach for Dilute Alloys. II. Noble and Transition Hosts

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Harrison's pseudopotential approach for noble and transition metals is generalized to discuss the corresponding alloys. In the noble-metal-based alloys, d-band effects are shown to be included in an effective nonlocal potential, the scattering equation for the pseudo-wave-function still being free-electron-like. In transition-metal alloys, s-d mixing and s-s corrections are introduced in a perturbative scheme, to the pure d-d scattering problem described in the tight-binding approximation. In both cases the contributions from host-metal-induced and impurity-induced s-d mixing are clearly separated.

I. INTRODUCTION

In a previous paper[1] (referred to as I) the case of non-noble-, non-transition-metal alloys was discussed within a pseudopotential approach, paying special attention to node effects. In that case the electronic structure of the host was characterized by a broad conduction band and a set of atomiclike narrow bands derived from inner-shell states (Fig. 1). The node effects discussed there involved essentially orthogonalization effects introduced by the extra atomic states associated with the impurity (cf. Fig. 1).

The main difference between noble, transition, and normal metals lies in the existence of a d band (filled in the case of noble metals and partially filled for the transition metals) in the neighborhood of the Fermi level (cf. Figs. 2 and 3).

These d states introduce further difficulties in the discussion of the alloy electronic structures even in the absence of node effects, so in this work we restrict ourselves to the simplest case of dominant charge effects. The pseudopotential theory for noble- and transition-metal hosts has been recently discussed by Harrison,[2] and the main point of the approach is to realize that tight-binding sums

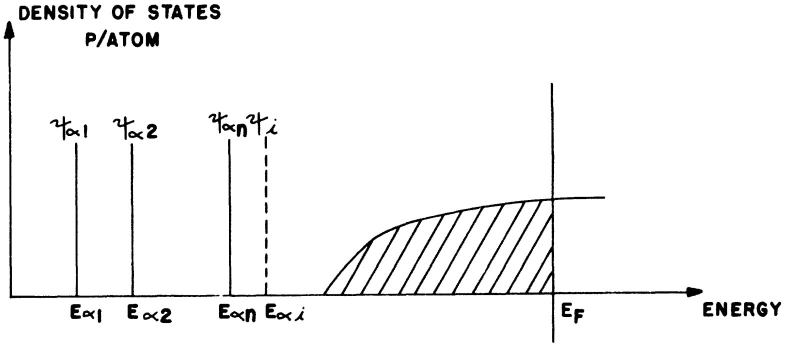


FIG. 1. Non-noble, non-transition-metal case (schematic).

constructed from atomic *d* states are not exact solutions of the complete crystal problem. From Harrison's developments it follows that for noble metals, for instance, *s*-*d* mixing effects appear to play an important role for states near the top of the tight-binding *d* band. It is expected, then, that impurity-induced rearrangements of the *d* density of states near the top of the *d* band may have important consequences in discussing isomer shifts. It is the purpose of this work to generalize the methods discussed in I to the case of noble and transition metals. At this point it is important to distinguish clearly the approaches to describing noble and transition metals. In fact, in noble-metal cases one has for the states in the neighborhood of the Fermi level (and these are the important states for alloying purposes) a dominant *s*-like character, *d*-band contributions appearing only through *s*-*d* mixing effects. On the other hand, for the transition-metal case the dominant contribution comes from *d*-like states obtained from tight-binding sums as far as host and alloy cases are concerned.[3]

It seems natural then in the case of noble metals to use an equivalent problem approach where the *d*-*d* scattering and *s*-*d* mixing effects appear as an effective nonlocal potential, introducing scattering on the plane-wave states. On the contrary, for transition-metal alloys, one expects that *s*-*d* mixing effects appear as a perturbation to the pure *d*-alloy scattering problem as defined previously,[3] so one obtains for the alloy problem a close parallelism between this case and Harrison's transition-metal-host problem.

To summarize: For noble-metal alloys again one starts by defining the "true" scattering problem, the corresponding pseudo-wave-function, and the effective impurity potential. The main difference from normal metals is provided by this effective potential since now the effects of *d*-*d* scattering and *s*-*d* mixing are all incorporated into the potential, the scattering equation for the pseudo-wave-function remaining free-electron-like as in normal metals.

A quite different approach should be used for transition metals: One starts with the pure *d*-*d* scattering problem defined in terms of tight-binding sums as the zeroth order terms[3]; *s*-*d* mixing is then allowed to introduce corrections exactly in the same way as in its pure-metal counterpart.[1] In this way in the limit of zero impurity perturbation one recovers Harrison's pseudopotential description of the transition-metal host.

II. FORMULATION OF IMPURITY PROBLEM FOR NOBLE-METAL CASE

We start by defining the alloy wave function, assuming from the beginning that node effects may be disregarded. The case of impurity and host belonging to different rows of the Periodic Table may

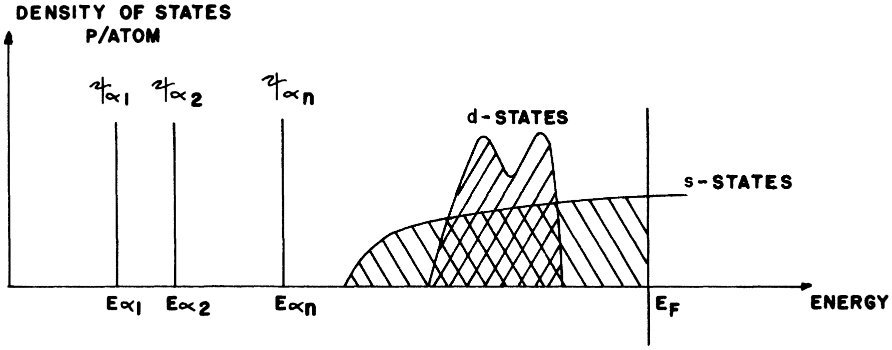


FIG. 2. Noble-metal case (schematic).

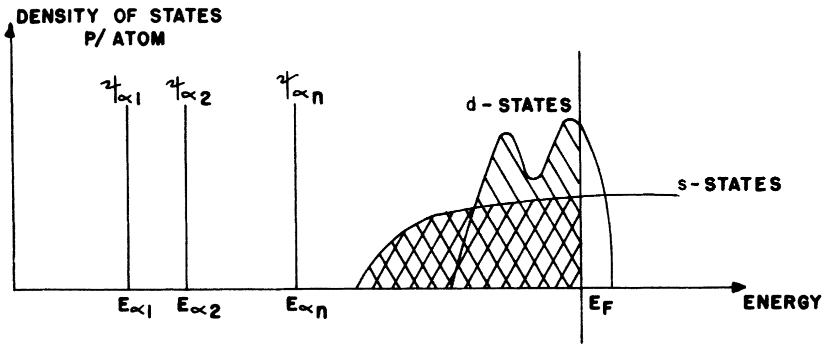


FIG. 3. Transition-metal case (schematic).

be handled along similar lines to those developed previously (see I); the only difference in comparison with normal metals is that d states must be included in considering the node effects. We define the "true" scattered wave function $|\psi_{\vec{k}}^{+}\rangle$ as a solution of

$$(T+V+U)|\psi_{\vec{k}}^{+}\rangle=E_{\vec{k}}|\psi_{\vec{k}}^{+}\rangle\ , \tag{1}$$

which must satisfy the following requirements:

(i) The scattered wave function must be orthogonal to all inner-shell states (assumed here to be identical to those of the pure metal):

$$\langle\alpha|\psi_{\vec{k}}^{+}\rangle=0 \tag{2}$$

for all states $|\alpha\rangle$.

(ii) It reduces in the limit of zero perturbation to the host-metal value:

$$\lim|\psi_{\vec{k}}^{+}\rangle=|\psi_{\vec{k}}\rangle \quad \text{as } U\to 0\ . \tag{3}$$

(iii) It shows an outgoing behavior typical of the scattering problem.

A very convenient way of writing $|\psi_{\vec{k}}^{+}\rangle$ is provided[2] by expanding in terms of an overcomplete set of plane waves and tight-binding d states. In doing so, one automatically fulfills condition (i) since for

$$|\psi_{\vec{k}}^{+}\rangle=(1-\sum_{\alpha}|\alpha\rangle\langle\alpha|)|\phi_{\vec{k}}^{+}\rangle+\sum_{d'}a_{d'}^{(+)}|d'\rangle\ , \tag{4}$$

one has $\langle\alpha|\psi_{\vec{k}}^{+}\rangle=0$ for all states $|\alpha\rangle$ since tight-binding states $|d'\rangle$ are orthogonal to the inner-shell states $|\alpha\rangle$ ($\langle\alpha|d'\rangle=0$ for all $|\alpha\rangle$, $|d'\rangle$). Expression (4) is formally similar to Harrison's wave function for the pure noble metal, but here the determination of the $\{a_d^{+}\}$ coefficients involves the solution of a pure-d impurity problem as will be discussed below. The existence of admixed d states in the pure-metal case is connected[2] with the fact that tight-binding sums constructed from atomic d orbitals are not exact solutions of the crystal Schrödinger equation. The mixing arises through a potential defined by Harrison as

$$\Delta|d\rangle=\delta V|d\rangle-\langle d|\delta V|d\rangle\,|d\rangle\ , \tag{5}$$

the potential δV being the difference between the actual self-consistent crystal potential V and an "atomic" potential V_a, from which the d states are derived.

The role of d states in the impurity problem for noble metals may be understood physically in the following way. Suppose there is a repulsive potential, for instance. When acting on d states, this potential, depending on its strength, may pile up states at the top of the d band or extract a d bound state above it. In both cases, because of s-d mixing [impurity induced or through the mixing potential (5)], one has an enhancement of the d character at the Fermi level or the appearance (in the case of d bound states) of a virtual bound state. These ideas will become clearer with the calculation of the $\{a_d^{(+)}\}$ coefficients and the definition of the equivalent equation. Now we proceed with the details of the calculation of $\{a_d^{(+)}\}$. Substituting (4) in (1), one gets

$$\begin{aligned}(T+V)|\phi_{\vec{k}}^{+}\rangle-\sum_{\alpha}E_{\alpha}|\alpha\rangle\langle\alpha|\phi_{\vec{k}}^{+}\rangle+\sum_{d'}a_{d'}^{(+)}(T+V)|d'\rangle\\ +U(1-\sum_{\alpha}|\alpha\rangle\langle\alpha|)|\phi_{\vec{k}}^{+}\rangle+\sum_{d'}a_{d'}^{(+)}U|d'\rangle\\ =E_{\vec{k}}|\phi_{\vec{k}}^{+}\rangle-\sum_{\alpha}E_{\vec{k}}|\alpha\rangle\langle\alpha|\phi_{\vec{k}}^{+}\rangle+\sum_{d'}E_{\vec{k}}a_{d'}^{(+)}|d'\rangle\ ,\end{aligned} \tag{6}$$

where in the absence of node effects we used

$$(T+V)|\alpha\rangle=E_{\alpha}|\alpha\rangle\ . \tag{7}$$

Now Eq. (6) must be multiplied by a particular d state in order to obtain an equation determining $a_{d}^{(+)}$. In doing so we use the following relations derived by Harrison[2]:

$$\langle d|T+V|\phi_{\vec{k}}^{+}\rangle=E_d\langle d|\phi_{\vec{k}}^{+}\rangle-\langle d|\Delta|\phi_{\vec{k}}^{+}\rangle\ , \tag{8a}$$

which follows from

$$(T+V)|d\rangle=E_d|d\rangle-\Delta|d\rangle\ , \tag{8b}$$

where

$$E_d=\langle d|T+V|d\rangle\ , \tag{8c}$$

the mixing potential Δ being defined by Eq. (5). It follows also from (8b) that

$$\langle d|\,T+V\,|d'\rangle = E_d\,\delta_{dd'} - \langle d|\,\Delta\,|d'\rangle \tag{8d}$$

and

$$\sum_{d'} \alpha_{d'}\,\langle d|\,\Delta\,|d'\rangle = 0 \tag{8e}$$

for any c numbers $\{\alpha_{d'}\}$, using the tight-binding approximations. Performing the calculation through these steps one gets

$$\begin{aligned}\langle d|\,T+V\,|\phi^{(+)}_{\vec{k}}\rangle &+ \sum_{d'} a^{+}_{d'}\langle d|\,T+V\,|d'\rangle \\ &+ \langle d|\,U(1-\sum_{\alpha}|\alpha\rangle\langle\alpha|)\,|\phi^{+}_{\vec{k}}\rangle \\ &+ \sum_{d'} a^{(+)}_{d'}\langle d|\,U\,|d'\rangle = E_{\vec{k}}\langle d|\phi^{+}_{\vec{k}}\rangle + E_{\vec{k}}\,a^{(+)}_{d}\,,\end{aligned} \tag{9}$$

where use was made of $\langle\alpha|d\rangle = 0$ for any $|\alpha\rangle$ and $|d\rangle$. Using Eqs. (8a), (8d), and (8e), one rewrites (9) as

$$\begin{aligned}E_d\langle d|\phi^{+}_{\vec{k}}\rangle &- \langle d|\,\Delta\,|\phi^{+}_{\vec{k}}\rangle + E_d\,a^{(+)}_{d} \\ &+ \langle d|\,U(1-\sum_{\alpha}|\alpha\rangle\langle\alpha|)\,|\phi^{+}_{\vec{k}}\rangle \\ &+ \sum_{d'} a^{(+)}_{d'}\langle d|\,U\,|d'\rangle = E_{\vec{k}}\langle d|\phi^{+}_{\vec{k}}\rangle + E_{\vec{k}}\,a^{(+)}_{d}\,.\end{aligned} \tag{10}$$

Rearranging terms one gets

$$\begin{aligned}(E_{\vec{k}} - E_d)\,a^{(+)}_{d} &= (E_d - E_{\vec{k}})\langle d|\phi^{+}_{\vec{k}}\rangle - \langle d|\,\Delta\,|\phi^{+}_{\vec{k}}\rangle \\ &+ \langle d|\,U(1-\sum_{\alpha}|\alpha\rangle\langle\alpha|)\,|\phi^{+}_{\vec{k}}\rangle + \sum_{d'} a^{(+)}_{d'}\langle d|\,U\,|d'\rangle\end{aligned} \tag{11}$$

or finally

$$\begin{aligned}a^{(+)}_{d} &= -\langle d|\phi^{+}_{\vec{k}}\rangle + \frac{\langle d|\Delta|\phi^{+}_{\vec{k}}\rangle}{E_d - E_{\vec{k}}} \\ &+ \frac{\langle d|U(1-\sum_{\alpha}|\alpha\rangle\langle\alpha|)|\phi^{+}_{\vec{k}}\rangle}{E_{\vec{k}} - E_d} \\ &+ \frac{1}{E_{\vec{k}} - E_d}\sum_{d'} a^{(+)}_{d'}\langle d|\,U\,|d'\rangle\;.\end{aligned} \tag{12}$$

Equation (12) solved for the unknowns $\{a^{(+)}_{d}\}$ provides the solution of the first step of the equivalent-equation approach for noble metals, since it is clear from (12) that the $\{a^{(+)}_{d}\}$ are obtained in terms of $|\phi^{+}_{\vec{k}}\rangle$, which when substituted into (6) provide an equation for the scattered pseudo-wave-function. This means that Eq. (12) incorporates the solution of the pure-d impurity problem and how d states mix with conduction states. In order to get a better feeling of things involved in Eq. (12) it is interesting to recover the pure-metal limit derived by Harrison by just taking $U=0$ in the equation defining the $a^{(+)}_{d'}$'s. If one calls $|\phi_{\vec{k}}\rangle$ the pure-metal ($U=0$) limit of the scattered pseudo-wave-functions and the corresponding coefficients $\{a_d\}$, one gets from (12)

$$a_d = -\langle d|\phi_{\vec{k}}\rangle + \frac{\langle d|\Delta|\phi_{\vec{k}}\rangle}{E_d - E_{\vec{k}}}\;. \tag{13}$$

Substituting (13) into (4) one obtains the pure-metal "true" wave function

$$\begin{aligned}|\psi_{\vec{k}}\rangle &= (1-\sum_{\alpha}|\alpha\rangle\langle\alpha|)\,|\phi_{\vec{k}}\rangle - \sum_{d'}|d'\rangle\langle d'|\phi_{\vec{k}}\rangle \\ &\qquad + \sum_{d'}\frac{|d'\rangle\langle d'|\Delta|\phi_{\vec{k}}\rangle}{E_{d'} - E_{\vec{k}}} \\ &= (1-\sum_{\alpha}|\alpha\rangle\langle\alpha| - \sum_{d'}|d'\rangle\langle d'|)\,|\phi_{\vec{k}}\rangle \\ &\qquad + \sum_{d'}\frac{|d'\rangle\langle d'|\Delta|\phi_{\vec{k}}\rangle}{E_{d'} - E_{\vec{k}}}\;.\end{aligned} \tag{14}$$

This expression provides a very simple interpretation of the first two terms of (12). The first term $-\langle d|\phi_{\vec{k}}\rangle$ is just the orthogonalization contribution of the d states as it occurs in the normal metal, and as if tight-binding sums were *solutions* of the exact crystal Hamiltonian. The second term of (12) is then the mixing term responsible for the occurrence of a d-like character in the conduction states. It must be emphasized that if $V=V_a$ (atomic d states exact solutions of the crystal problem) then by (5) it follows that $\Delta=0$ and the wave function (14) is reduced to a normal-metal-type wave function.

Now we are in a position to discuss the meaning of the remaining terms of Eq. (12). The third term of (12) describes impurity s-d mixing, which compares formally to the second term just by replacing the mixing potential Δ by the "reduced" impurity potential $U(1-\sum_{\alpha}|\alpha\rangle\langle\alpha|)$. Finally, the last term describes pure d-d scattering, which is responsible for piling up d states at the top of the band or for the existence of a d bound state outside the d band. Solving Eq. (12) for the coefficients $\{a^{(+)}_{d}\}$ is then equivalent to solving the pure d-d impurity problem defined by matrix elements $\langle d|U|d'\rangle$. At this point we introduce for simplicity the approximation of localized impurity potentials for which $\langle d|U|d'\rangle \cong \tilde{U}$, where $\tilde{U}$ is independent of d, d'. Within this approximation it is possible to obtain a rather simple expression for the $\{a^{(+)}_{d}\}$ coefficients without disturbing significantly the physics of the problem. It follows then from (12) that

$$\begin{aligned}\sum_{d'} a^{(+)}_{d'} &= -\sum_{d'}\langle d'|\phi^{+}_{\vec{k}}\rangle + \sum_{d'}\frac{\langle d'|\Delta|\phi^{+}_{\vec{k}}\rangle}{E_{d'} - E_{\vec{k}}} \\ &+ \sum_{d'}\frac{\langle d'|U(1-\sum_{\alpha}|\alpha\rangle\langle\alpha|)|\phi^{+}_{\vec{k}}\rangle}{E_{\vec{k}} - E_{d'}} \\ &+ \tilde{U}\sum_{d}\frac{1}{E_{\vec{k}} - E_d}\sum_{d'} a^{(+)}_{d'}\;.\end{aligned} \tag{15}$$

Introducing the function $F(E)$ defined by

$$F(E)=\textstyle\sum_d 1/(E-E_d)\ ,$$

it follows from (15) that

$$\sum_{d'} a_{d'}^{(+)}=\frac{1}{1-\tilde{U}F(E_{\vec{k}})}\left(-\sum_{d'}\langle d'|\phi_{\vec{k}}^{+}\rangle+\sum_{d'}\frac{\langle d'|\Delta|\phi_{\vec{k}}^{+}\rangle}{E_{d'}-E_{\vec{k}}}+\sum_{d'}\frac{\langle d'|U(1-\sum_\alpha|\alpha\rangle\langle\alpha|)|\phi_{\vec{k}}^{+}\rangle}{E_{\vec{k}}-E_{d'}}\right)\ . \tag{16}$$

Combining Eqs. (16) and (12), in the localized-impurity-potential approximation it follows finally that the coefficients $\{a_d^{(+)}\}$ are

$$a_d^{(+)}=-\langle d|\phi_{\vec{k}}^{+}\rangle+\frac{\langle d|\Delta|\phi_{\vec{k}}^{+}\rangle}{E_d-E_{\vec{k}}}+\frac{\langle d|U(1-\sum_\alpha|\alpha\rangle\langle\alpha|)|\phi_{\vec{k}}^{+}\rangle}{E_{\vec{k}}-E_d}+\frac{\tilde{U}}{(E_{\vec{k}}-E_d)[1-\tilde{U}F(E_{\vec{k}})]}$$

$$\times\left(-\sum_{d'}\langle d'|\phi_{\vec{k}}^{+}\rangle+\sum_{d'}\frac{\langle d'|\Delta|\phi_{\vec{k}}^{+}\rangle}{E_{d'}-E_{\vec{k}}}+\sum_{d'}\frac{\langle d'|U(1-\sum_\alpha|\alpha\rangle\langle\alpha|)|\phi_{\vec{k}}^{+}\rangle}{E_{\vec{k}}-E_{d'}}\right)\ . \tag{17}$$

Expression (17) can be rewritten in a more practical way if one calculates the total contribution $\sum_d a_d^{(+)}|d\rangle$ of the d states to the scattered wave function. Using the approximation $\tilde{U}\cong\langle d|U|d'\rangle$, one gets

$$\sum_d a_d^{(+)}|d\rangle=\left(-\sum_d|d\rangle\langle d|+\sum_d\frac{|d\rangle\langle d|\Delta}{E_d-E_{\vec{k}}}+\sum_d\frac{|d\rangle\langle d|U(1-\sum_\alpha|\alpha\rangle\langle\alpha|)}{E_{\vec{k}}-E_d}\right)|\phi_{\vec{k}}^{+}\rangle$$

$$+\sum_d\frac{|d\rangle\langle d|U}{(E_{\vec{k}}-E_d)[1-\tilde{U}F(E_{\vec{k}})]}\times\left(-\sum_{d'}|d'\rangle\langle d'|+\sum_{d'}\frac{|d'\rangle\langle d'|\Delta}{E_{d'}-E_{\vec{k}}}+\sum_{d'}\frac{|d'\rangle\langle d'|U(1-\sum_\alpha|\alpha\rangle\langle\alpha|)}{E_{\vec{k}}-E_{d'}}\right)|\phi_{\vec{k}}^{+}\rangle\ . \tag{18a}$$

Expression (18a) shows the connection between the d-like part of the scattering wave function $\sum_d a_d^{(+)}|d\rangle$ and the scattered pseudo-wave-function $|\phi_{\vec{k}}^{+}\rangle$. When $|\phi_{\vec{k}}^{+}\rangle$ is known, together with the self-consistent impurity potential U, one obtains directly the d part through the expression

$$\textstyle\sum_d a_d^{(+)}|d\rangle=(\text{operator})|\phi_{\vec{k}}^{+}\rangle\ , \tag{18b}$$

where the (operator) above is defined by the terms in large parentheses in (18a), which depend only on tight-binding sums and energies, core states, and the impurity potential U. These equations are also the central step for obtaining the equivalent scattering equation for $|\phi_{\vec{k}}^{+}\rangle$ because of its special form (18b). The next step is to obtain the equivalent equation for the scattered pseudo-wave-function $|\phi_{\vec{k}}^{+}\rangle$. To do this we return to Eq. (6), which is now rewritten as

$$[T+V+\textstyle\sum_\alpha(E_{\vec{k}}-E_\alpha)|\alpha\rangle\langle\alpha|\,]\,|\phi_{\vec{k}}^{+}\rangle$$

$$+\textstyle\sum_d a_d^{(+)}(E_d-\Delta)|d\rangle-\sum_d E_{\vec{k}}a_d^{(+)}|d\rangle$$

$$+U(1-\textstyle\sum_\alpha|\alpha\rangle\langle\alpha|)|\phi_{\vec{k}}^{+}\rangle+\sum_d a_d^{(+)}U|d\rangle$$

$$=E_{\vec{k}}|\phi_{\vec{k}}^{+}\rangle\ . \tag{19}$$

Expression (19) is written in such a way that the first three terms contain nonvanishing contributions in the limit $U\rightarrow 0$ and the last two terms are pure impurity effects. Now we calculate the terms $\sum_d a_d^{(+)}(E_d-\Delta)|d\rangle$ and $\sum_d E_{\vec{k}}a_d^{(+)}|d\rangle$ using expression (18); according to this expression, in $\sum_d a_d^{(+)}|d\rangle$ there are terms independent of U, which describe pure-metal effects and the impurity-dependent terms which we call $\sum_d a_d^{(+)}(U)|d\rangle$. In the calculation of the above terms we insert explicitly for $\sum_d a_d^{(+)}|d\rangle$ only the impurity-independent terms, keeping the remaining terms as $a_d^{(+)}(U)$. In this way one gets

$$\sum_d a_d^{(+)}(E_d-\Delta)|d\rangle=\left(-\sum_d(E_d-\Delta)|d\rangle\langle d|+\sum_d\frac{(E_d-\Delta)|d\rangle\langle d|\Delta}{E_d-E_{\vec{k}}}\right)|\phi_{\vec{k}}^{+}\rangle+\sum_d a_d^{(+)}(U)(E_d-\Delta)|d\rangle\ . \tag{20a}$$

$$\sum_d E_{\vec{k}}a_d^{(+)}|d\rangle=\left(-\sum_d E_{\vec{k}}|d\rangle\langle d|+\sum_d\frac{E_{\vec{k}}|d\rangle\langle d|}{E_d-E_{\vec{k}}}\right)|\phi_{\vec{k}}^{+}\rangle+\sum_d a_d^{(+)}(U)E_{\vec{k}}|d\rangle\ . \tag{20b}$$

Substituting (20a) and (20b) into (19) one obtains

$$\left(T+V+\sum_\alpha(E_{\vec{k}}-E)|\alpha\rangle\langle\alpha|\right)|\phi_{\vec{k}}^{+}\rangle+\left(-\sum_d(E_d-\Delta)|d\rangle\langle d|+\sum_d E_{\vec{k}}|d\rangle\langle d|+\sum_d\frac{(E_d-E_{\vec{k}}-\Delta)|d\rangle\langle d|\Delta}{E_d-E_{\vec{k}}}\right)|\phi_{\vec{k}}^{+}\rangle$$

$$+\sum_d a_d^{(+)}(U)(E_d-\Delta)|d\rangle-\sum_d a_d^{(+)}(U)E_{\vec{k}}|d\rangle+U\left(1-\sum_\alpha|\alpha\rangle\langle\alpha|\right)|\phi_{\vec{k}}^{+}\rangle+\sum_d a_d^{(+)}U|d\rangle=E_{\vec{k}}|\phi_{\vec{k}}^{+}\rangle\ . \tag{21}$$

The first two terms of (21) can be rearranged to reproduce the pure-noble-metal pseudo-Hamiltonian derived by Harrison[2]; one obtains for these terms

$$\Big(T+V+\sum_{\alpha}(E_{\vec k}-E_{\alpha})|\alpha\rangle\langle\alpha| + \sum_{d}(E_{\vec k}-E_{d})|d\rangle\langle d| + \sum_{d}\Delta|d\rangle\langle d| + \sum_{d}|d\rangle\langle d|\Delta + \sum_{d}\frac{\Delta|d\rangle\langle d|\Delta}{E_{\vec k}-E_{d}}\Big)|\phi^{+}_{\vec k}\rangle = \mathcal{H}^{P}_{\text{nob}}|\phi^{+}_{\vec k}\rangle\ . \tag{22}$$

Using this result, Eq. (21) can be rewritten as

$$(E_{\vec k}-\mathcal{H}^{P}_{\text{nob}})|\phi^{+}_{\vec k}\rangle = U(1-\textstyle\sum_{\alpha}|\alpha\rangle\langle\alpha|)|\phi^{+}_{\vec k}\rangle + \textstyle\sum_{d}a_{d}^{(+)}(U)(E_{d}-E_{\vec k}-\Delta)|d\rangle + \textstyle\sum_{d}a_{d}^{(+)}U|d\rangle\ . \tag{23}$$

III. DETERMINATION OF EFFECTIVE IMPURITY POTENTIAL AND EQUIVALENT SCATTERING EQUATION

The effective impurity potential is defined in the following way:

$$U^{P}|\phi^{+}_{\vec k}\rangle = \text{right-hand side of (23)}.$$

More explicitly one gets

$$U^{P}|\phi^{+}_{\vec k}\rangle = U\Big(1-\sum_{\alpha}|\alpha\rangle\langle\alpha|\Big)|\phi^{+}_{\vec k}\rangle + \sum_{d}\Big(-U|d\rangle\langle d| + \frac{U|d\rangle\langle d|\Delta}{E_{d}-E_{\vec k}}\Big)|\phi^{+}_{\vec k}\rangle + \sum_{d}a_{d}^{(+)}(U)(E_{d}-E_{\vec k}-\Delta+U)|d\rangle\ , \tag{24}$$

where in the last term of the right-hand side of (23) the impurity-independent terms were separated from the $a_{d}^{(+)}(U)$ terms. It turns out from (24) that the first two contributions to the effective potential are given by

$$U\Big(1-\sum_{\alpha}|\alpha\rangle\langle\alpha| - \sum_{d}|d\rangle\langle d|\Big) + \sum_{d}\frac{U|d\rangle\langle d|\Delta}{E_{d}-E_{\vec k}}\ . \tag{25}$$

These terms do not involve explicitly the d-d scattering which is contained in the last terms of (24). Using Eq. (18), we calculate

$$\sum_{d}a_{d}^{(+)}(U)(E_{d}-E_{\vec k}-\Delta+U)|d\rangle = \Big(\sum_{d}\frac{(E_{d}-E_{\vec k}-\Delta+U)|d\rangle\langle d|U(1-\sum_{\alpha}|\alpha\rangle\langle\alpha|)}{E_{\vec k}-E_{d}}\Big)|\phi^{+}_{\vec k}\rangle + \sum_{d}\frac{(E_{d}-E_{\vec k}-\Delta+U)|d\rangle\langle d|U}{(E_{d}-E_{\vec k})[1-\tilde U F(E_{\vec k})]}\Big(-\sum_{d'}|d'\rangle\langle d'| + \sum_{d'}\frac{|d'\rangle\langle d'|\Delta}{E_{d'}-E_{\vec k}} + \sum_{d'}\frac{|d'\rangle\langle d'|U(1-\sum_{\alpha}|\alpha\rangle\langle\alpha|)}{E_{\vec k}-E_{d'}}\Big)|\phi^{+}_{\vec k}\rangle. \tag{26}$$

Using (25) and (26) one obtains finally for the effective impurity potential

$$U^{P} = U\Big(1-\sum_{\alpha}|\alpha\rangle\langle\alpha| - \sum_{d}|d\rangle\langle d|\Big) + \sum_{d}\frac{U|d\rangle\langle d|\Delta}{E_{d}-E_{\vec k}} + \sum_{d}\frac{(E_{d}-E_{\vec k}-\Delta+U)|d\rangle\langle d|U(1-\sum_{\alpha}|\alpha\rangle\langle\alpha|)}{E_{\vec k}-E_{d}} + \sum_{d}\frac{(E_{\vec k}-E_{d}-\Delta+U)|d\rangle\langle d|U}{(E_{d}-E_{\vec k})[1-\tilde U F(E_{\vec k})]}\Big(-\sum_{d'}|d'\rangle\langle d'| + \sum_{d'}\frac{|d'\rangle\langle d'|\Delta}{E_{d'}-E_{\vec k}} + \sum_{d'}\frac{|d'\rangle\langle d'|U(1-\sum_{\alpha}|\alpha\rangle\langle\alpha|)}{E_{\vec k}-E_{d'}}\Big). \tag{27}$$

Using the U^{P} defined in such a way, the scattering equation for the pseudo-wave-function becomes

$$(E_{\vec k}-\mathcal{H}^{P}_{\text{nob}})|\phi^{+}_{\vec k}\rangle = U^{P}|\phi^{+}_{\vec k}\rangle \tag{28}$$

or incorporating the outgoing behavior and the condition

$$\lim|\phi^{+}_{\vec k}\rangle = |\phi_{\vec k}\rangle \quad \text{as } U\to 0\ ,$$

one obtains the equivalent Lippman-Schwinger equation:

$$|\phi^{+}_{\vec k}\rangle = |\phi_{\vec k}\rangle + (E_{\vec k}-\mathcal{H}^{P}_{\text{nob}}+i\epsilon)^{-1}U^{P}|\phi^{+}_{\vec k}\rangle\ . \tag{29}$$

When Eq. (29) is solved in terms of the impurity potential U, using Eqs. (4) and (12) one obtains the "true" scattering wave function. The self-consistent solution is then obtained using the same methods as in I.

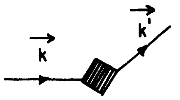
IV. INTERPRETATION OF EFFECTIVE POTENTIAL

The equivalent problem defined by Eqs. (29) and (27) provides a clear picture of the scattering mechanisms involving d electrons in the noble-metal case. These mechanisms are all contained in the effective potential since the effective scattering equation is free-electron-like, assuming as in I that $|\phi_{\vec k}\rangle$ is reasonably represented by a single plane wave. From Eq. (27), one sees that the matrix elements of U^{P} between plane waves, $\langle\vec k'|U^{P}|\vec k\rangle$, involve several contributions (cf. the Appendix).

To put our result in pictorial terms we introduce the following elementary scattering processes:

(a) the direct scattering from $\vec k$ to $\vec k'$ in the presence of a reduction factor

$$(1-\textstyle\sum_{\alpha}|\alpha\rangle\langle\alpha| - \sum|d\rangle\langle d|)$$



$$\equiv \langle \vec{k}' | U \Big(1 - \sum_{\alpha} |\alpha\rangle\langle\alpha| - \sum_{d} |d\rangle\langle d|\Big) |\vec{k}\rangle$$

FIG. 4. Direct scattering from *k* to *k'*, in the presence of a reduction factor $(1-\sum_\alpha |\alpha\rangle\langle\alpha| - \sum |d\rangle\langle d|)$ as in the case of normal metals without node effects.

as in the case of normal metals without node effects (as it should be if tight-binding states were exact states of the crystal Hamiltonian) (see Fig. 4); (b) bare scattering by the impurity potential U (Fig. 5); (c) host-metal s-d mixing inducing s-d scattering (Fig. 6); (d) the impurity-induced s-d mixing effects, reduced by inner-shell orthogonalization (Fig. 7); and (e) the matrix elements $\langle \vec{k} | d \rangle$ (Fig. 8). Using this notation it is possible to describe the processes involving d-d scattering. Typical examples are provided by the last terms of (27).

In fact, an s-d mixing involving d-d scattering can be depicted in terms of the processes represented in Fig. 9. The occurrence of the factor $1 - UF(E_{\vec{k}})$ characterizes the usual d-d scattering problem. From this factor one knows if there exist impurity-extracted d bound states which appear in Anderson's model[4] of the impurity problem.

Using this notation, the effective-potential matrix elements can be analyzed as shown in Fig. 10.

V. FORMULATION OF IMPURITY PROBLEM FOR TRANSITION-METAL CASE

A. Pure-Metal Results

At this point it is worthwhile to summarize Harrison's main results for the pure-transition host. If we call $|d\rangle$ the tight-binding sum corresponding to d states, then the "true" wave function for energies in the d-like region reads

$$|\psi_d\rangle = |d\rangle + \big(1 - \textstyle\sum_\alpha |\alpha\rangle\langle\alpha|\big)|\phi\rangle \ , \qquad (30)$$

where the pseudo-wave-function $|\phi\rangle$ is defined as

$$|\phi\rangle = \textstyle\sum_{\vec{k}} a_{\vec{k}} |\vec{k}\rangle \ . \qquad (31)$$

Substituting (30) in the Schrödinger equation and using (5), (7), (8b), and (8c), one gets for $|\phi\rangle$

$$(T+V)|\phi\rangle + \textstyle\sum_\alpha (E-E_\alpha)|\alpha\rangle\langle\alpha|\phi\rangle + (E_d - E - \Delta)|d\rangle = E|\phi\rangle \ . \qquad (32)$$

Equation (32) is now solved within a perturbation approach in powers of the s-d mixing parameter Δ; one starts from the following equation [obtained substituting (31) into (32)]:

$$\sum_{\vec{k}'} a_{\vec{k}'}\left(\frac{\vec{k}'^2}{2m} - E\right)|\vec{k}'\rangle + \sum_{\vec{k}'} a_{\vec{k}'} V|\vec{k}'\rangle + \sum_{\vec{k}',\alpha} a_{\vec{k}'}(E-E_\alpha) \times |\alpha\rangle\langle\alpha|\vec{k}'\rangle + (E_d - E - \Delta)|d\rangle = 0 \ , \qquad (33)$$

to obtain (for instance to first order in Δ)

$$a_{\vec{k}} \simeq -\langle\vec{k}|\Delta|d\rangle/(E_d - E_{\vec{k}}) \ ,$$

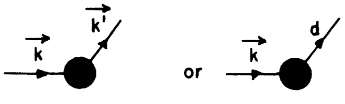
$E_{\vec{k}}$ being defined as

$$E_{\vec{k}} = \vec{k}^2/2m + \langle\vec{k}|W|\vec{k}\rangle$$

where W is Harrison's[2] pseudopotential for noble metals. It will turn out in the following that Eq. (33) plays an essential role in incorporating boundary conditions (zero-impurity potential limit) in the scattering problem.

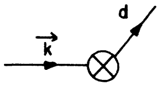
B. Definition of Impurity Problem

One starts incorporating in the problem three different aspects. First, the orthogonality condition involving the inner-shell states must be automatically ensured; in the present case it will be assumed that the impure-metal core states are not very much perturbed by the impurity (charge effects dominant). Second, since in the limit of zero s-d mixing, Eq. (30) for $|\psi_d\rangle$ reduces to the tight-binding limit $|d\rangle$, the condition will be imposed that the scattering solution $|\psi_d^+\rangle$ be the sum of a dominant tight-binding-like solution of the impurity problem plus plane-wave corrections through impurity- and host-metal-induced s-d mixing. Finally, the new pseudo-wave-function $|\phi^+\rangle$ involves also scattering requirements that imply outgoing behavior; also in the limit of vanishing perturbation it should reduce to the pure-metal limit (involving only host-metal s-d mixing effects). In conclusion, one describes the scattering problem through



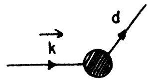
meaning $\langle \vec{k}' | U | \vec{k} \rangle$ and $\langle d' | U | \vec{k} \rangle$

FIG. 5. Rare scattering by the impurity potential U.



$$\equiv \frac{\langle d | \Delta | \vec{k} \rangle}{E_d - E_{\vec{k}}}$$

FIG. 6. Host-metal s-d mixing inducing s-d scattering.



$$\equiv \langle d|U(1-\sum_{\alpha}|\alpha\rangle\langle\alpha|)|\vec{k}\rangle$$

FIG. 7. Impurity-induced *s*-*d* mixing effects, reduced by inner-shell orthogonalization.

$$|\psi_d^{+}\rangle=\sum_{d'}a_{d'}^{(+)}|d'\rangle+\left(1-\sum_{\alpha}|\alpha\rangle\langle\alpha|\right)|\phi^{+}\rangle\ . \quad (34)$$

In Eq. (34) the coefficients $a_{d'}^{(+)}$ are the solution of the pure-metal tight-binding scattering problem[3] (cf. Sec. V C), and the scattering conditions read

$$a_{d'}^{(+)}=\delta_{dd'}+\delta a_{d'}^{(+)}\ , \quad (35)$$

where $\delta a_{d'}^{(+)}$ describes scattering and reduces to zero in the limit of zero perturbation. Quite similarly the scattered pseudo-wave-function is defined as

$$|\phi^{+}\rangle=\sum_{\vec{k}'}a_{\vec{k}'}^{(+)}|\vec{k}'\rangle\ . \quad (36)$$

The coefficients $a_{\vec{k}'}^{(+)}$ are defined as

$$a_{\vec{k}'}^{(+)}=a_{\vec{k}'}+\delta a_{\vec{k}'}^{(+)} \quad (37)$$

[the $a_{\vec{k}'}$ being the solutions of (30) and (33)] and correspond to the pure-metal limit. In these conditions Eq. (34) can be written as

$$|\psi_d^{(+)}\rangle=|d\rangle+\left(1-\sum_{\alpha}|\alpha\rangle\langle\alpha|\right)|\phi\rangle+\sum_{d'}\delta a_{d'}^{(+)}|d'\rangle$$
$$+\left(1-\sum_{\alpha}|\alpha\rangle\langle\alpha|\right)\sum_{\vec{k}'}\delta a_{\vec{k}'}^{(+)}|\vec{k}'\rangle\ . \quad (38)$$

Equation (38) shows the characteristic features of the problem; the first term is the pure-metal *d* wave function, the second and the third being, respectively, the scattered *d*-like states and the impurity admixed *s*-like states.

Finally, it should be emphasized that up to here only scattering states are considered. If the impurity perturbation is strong enough to extract *d* bound states from the *d* band, one should modify the proposed wave function (38).

C. Definition of Tight-Binding-Impurity Problem

First of all we introduce the tight-binding Hamiltonian defined by $\mathcal{H}^{\text{TB}}=T+V_a$, V_a being an atomic-like potential, from which the tight-binding density of states is derived. Now we introduce the self-consistent impurity potential U, which must be determined at the end of the calculation. The pure tight-binding-impurity problem is defined as

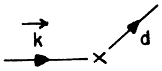


FIG. 8. Matrix elements $\langle k|d\rangle$.

$$|d^{+}\rangle=|d\rangle+(E-\mathcal{H}^{\text{TB}}+i\epsilon)^{-1}U|d^{+}\rangle\ , \quad (39)$$

with

$$|d^{+}\rangle=\sum_{d'}a_{d'}^{(+)}|d'\rangle,\quad a_{d'}^{(+)}=\delta_{dd'}+\delta a_{d'}^{(+)}$$

The general solution of the problem (39) is given in Ref. 3, and in the following the coefficients $a_{d'}^{(+)}$ will be supposed known as functions of U and of the density of states of the tight-binding *d* band.[3]

D. Determination of Scattered Pseudo-Wave-Function

One starts from the usual equation

$$(T+V+U)|\psi_d^{(+)}\rangle=E|\psi_d^{(+)}\rangle\ . \quad (40)$$

Substituting (34) in (40) one gets

$$(T+V)|\phi^{+}\rangle+U|\phi^{+}\rangle-\sum_{\alpha}(T+V)|\alpha\rangle\langle\alpha|\phi^{+}\rangle$$
$$-U\sum_{\alpha}|\alpha\rangle\langle\alpha|\phi^{+}\rangle+\sum_{d'}a_{d'}^{(+)}(T+V)|d'\rangle+\sum_{d'}a_{d'}^{(+)}U|d'\rangle$$
$$=\sum_{d'}a_{d'}^{(+)}E|d'\rangle+E|\phi^{+}\rangle-\sum_{\alpha}E|\alpha\rangle\langle\alpha|\phi^{+}\rangle\ . \quad (41)$$

Using Eqs. (7) and (8b) one has

$$\sum_{\alpha}(T+V)|\alpha\rangle\langle\alpha|\phi^{+}\rangle=\sum_{\alpha}E_{\alpha}|\alpha\rangle\langle\alpha|\phi^{+}\rangle\ , \quad (42a)$$

$$\sum_{d'}a_{d'}^{(+)}(T+V)|d'\rangle=\sum_{d'}a_{d'}^{(+)}(E_{d'}-\Delta)|d'\rangle\ . \quad (42b)$$

Combining (41), (42a), and (42b) one gets

$$\left(T+V+\sum_{\alpha}(E-E_{\alpha})|\alpha\rangle\langle\alpha|\right)|\phi^{+}\rangle$$
$$+U\left(1-\sum_{\alpha}|\alpha\rangle\langle\alpha|\right)|\phi^{+}\rangle$$

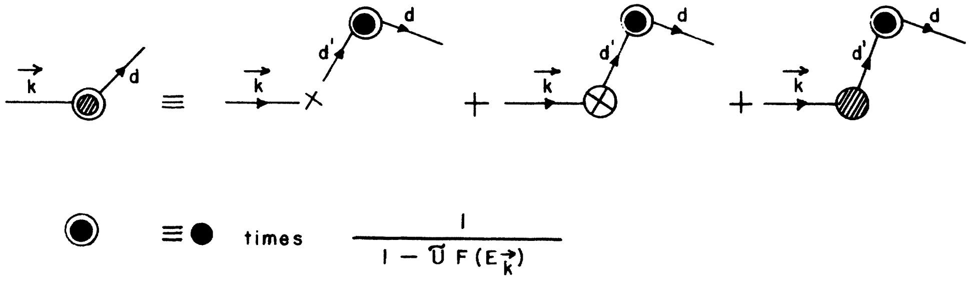


FIG. 9. *s*-*d* mixing involving *d*-*d* scattering.

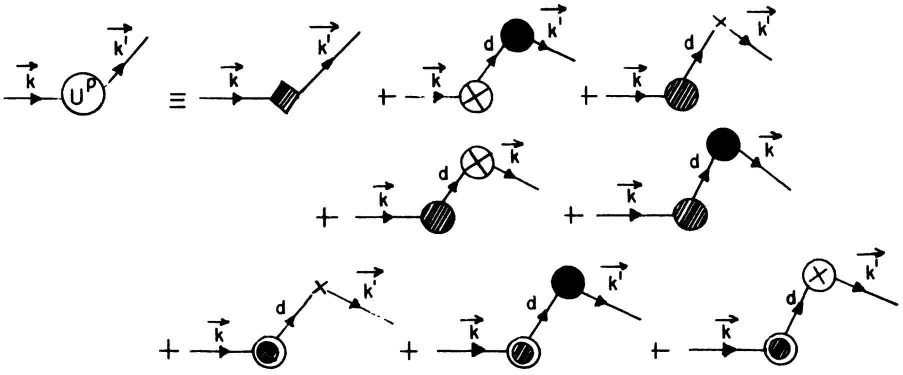


FIG. 10. Effective-potential matrix elements.

$$+\sum_{d'} a^{(+)}_{d'}(E_{d'} - E - \Delta)|d'\rangle$$

$$+\sum_{d'} a^{(+)}_{d'}(U|d'\rangle = E|\phi^{+}\rangle \quad . \tag{43}$$

At this point it is very convenient to use (35) in order to separate the impurity-dependent terms of $a^{(+)}_{d'}$; Eq. (43) becomes finally

$$\Big(T + V + \sum_{\alpha} (E - E_{\alpha})|\alpha\rangle\langle\alpha|\Big)|\phi^{+}\rangle$$
$$+ (E_d - E - \Delta)|d\rangle - E|\phi^{+}\rangle$$
$$+ U\Big(1 - \sum_{\alpha}|\alpha\rangle\langle\alpha|\Big)|\phi^{+}\rangle$$
$$+ \sum_{d'} \delta a^{(+)}_{d'}(U)(E_{d'} - E - \Delta)|d'\rangle$$
$$+ \sum_{d'} a^{(+)}_{d'} U|d'\rangle = 0 \quad . \tag{44}$$

The first three terms of Eq. (44), being the limit for zero impurity perturbation of the scattering equation for the pseudo-wave-function, coincide with the host-metal equation (32). The fourth term describes s-s scattering induced by the "reduced" impurity potential $U(1 - \sum_{\alpha}|\alpha\rangle\langle\alpha|)$. Finally the last two terms are s-d mixing terms involving, respectively, host-metal s-d mixing to scattered d-states and impurity-induced s-d mixing.

E. Solution of Scattering Equation by a Perturbation Approach

We first substitute Eq. (36) into Eq. (44) and define

$$W_0 = V + \textstyle\sum_{\alpha}(E - E_{\alpha})|\alpha\rangle\langle\alpha| \quad ,$$

to get

$$\sum_{\vec{k}'} a^{(+)}_{\vec{k}'}(T + W_0 - E_k)|\vec{k}'\rangle + (E_d - E_{\vec{k}} - \Delta)|d\rangle$$
$$+ \sum_{\vec{k}'} a^{(+)}_{\vec{k}'} U\Big(1 - \sum_{\alpha}|\alpha\rangle\langle\alpha|\Big)|\vec{k}'\rangle$$
$$+ \sum_{d'} \delta a^{(+)}_{d'}(U)(E_{d'} - E_{\vec{k}} - \Delta)|d'\rangle$$
$$+ U|d\rangle + \sum_{d'} \delta a^{(+)}_{d'}(U)\, U|d'\rangle = 0 \quad , \tag{45}$$

where we wish to emphasize that the coefficients $\delta a^{(+)}_{d'}(U)$ are known from a previous solution of the problem defined by (39). Since the zeroth-order solution of (45) must correspond to Harrison's determination of the s-d admixing coefficients $a_{\vec{k}'}$ of Eq. (37), we find from (45)

$$\sum_{\vec{k}'} a_{\vec{k}'}(T + W_0 - E_{\vec{k}})|\vec{k}'\rangle + (E_d - E_{\vec{k}} - \Delta)|d\rangle = 0 \quad , \tag{46}$$

the solutions being given by Harrison [first-order solution is exemplified in (34)]. Now it remains to determine the $a^{(+)}_{\vec{k}}$ coefficients in (37) in powers of the scattering potential. In order to do that one should realize that the first two terms of (45) just describe host-metal contributions, all scattering properties being contained in the remaining terms. Once one recognizes this, the first two terms may be replaced by

$$\sum_{\vec{k}'} \delta a^{(+)}_{\vec{k}'}(E_{\vec{k}'} - E_{\vec{k}})|\vec{k}'\rangle \quad , \tag{47}$$

where $E_{\vec{k}'}$, $E_{\vec{k}}$ are Harrison's renormalized energies due to s-d mixing. To summarize: One considers the scattering of s-d renormalized states by the impurity potential. Then to nth order in the perturbation U, one gets

$$\sum_{\vec{k}''} \delta a^{(+)(n)}_{\vec{k}''}(E_{\vec{k}''} - E_{\vec{k}})|\vec{k}''\rangle + \sum_{\vec{k}''} \delta a^{(+)(n-1)}_{\vec{k}''} U\Big(1 - \sum_{\alpha}|\alpha\rangle\langle\alpha|\Big)|\vec{k}''\rangle$$
$$+ \sum_{d'} \delta a^{(+)(n)}_{d'}(U)(E_{d'} - E_{\vec{k}} - \Delta)|d'\rangle + \sum_{d'} \delta a^{(+)(n-1)}_{d'}(U)U|d'\rangle = 0 \quad , \tag{48}$$

where $\delta a_{d'}^{(+)(n)}(U)$ is the *n*th order term of the expansion of the scattering T matrix[3] in powers of the impurity potential U. In expression (48), $\delta a_{\vec{k}''}^{(+)(0)} = a_{\vec{k}''}$, the solution of the pure-metal problem as given by Harrison. Multiplying everything by a state $|\vec{k}'\rangle$ one gets

$$\delta a_{\vec{k}'}^{(+)(n)} = \sum_{\vec{k}''} \delta a_{\vec{k}''}^{(+)(n-1)} \frac{\langle \vec{k}' | U(1-\sum_\alpha |\alpha\rangle\langle\alpha|) | \vec{k}''\rangle}{E_{\vec{k}} - E_{\vec{k}'} + i\epsilon} + \sum_{d'} \delta a_{d'}^{(+)(n)}(U) \frac{\langle \vec{k}' | E_{d'} - E_{\vec{k}} - \Delta | d'\rangle}{E_{\vec{k}} - E_{\vec{k}'} + i\epsilon} + \sum_{d'} \delta a_{d'}^{(+)(n-1)}(U) \frac{\langle \vec{k}' | U | d'\rangle}{E_{\vec{k}} - E_{\vec{k}'} + i\epsilon} \quad , \tag{49}$$

where the outgoing conditions are incorporated through the $+i\epsilon$ in the denominator ensuring that

$$\sum_{\vec{k}'} \delta a_{\vec{k}'}^{(+)(n)}(U) | \vec{k}'\rangle$$

has an outgoing behavior.

Finally, combining expression (49) with (38), one obtains for instance, to first order in impurity s-d mixing effects,

$$\begin{aligned} |\psi_d^+\rangle = {} & |d\rangle + \Big(1 - \sum_\alpha |\alpha\rangle\langle\alpha|\Big) |\phi\rangle + \sum_{d'} \delta a_{d'}^{(+)}(U) |d'\rangle \\ & + \Big(1 - \sum_\alpha |\alpha\rangle\langle\alpha|\Big) \Bigg[\sum_{\vec{k}'',\vec{k}'} a_{\vec{k}''} \frac{\langle \vec{k}' | U(1-\sum_\alpha |\alpha\rangle\langle\alpha|) | \vec{k}''\rangle}{E_{\vec{k}} - E_{\vec{k}'} + i\epsilon} |\vec{k}'\rangle \Bigg] \\ & + \Big(1 - \sum_\alpha |\alpha\rangle\langle\alpha|\Big) \Bigg[\sum_{\vec{k}',d'} \delta a_{d'}^{(1)}(U) \frac{\langle \vec{k}' | E_{d'} - E_{\vec{k}} - \Delta | d'\rangle}{E_{\vec{k}} - E_{\vec{k}'} + i\epsilon} |\vec{k}'\rangle \Bigg] \\ & + \Big(1 - \sum_\alpha |\alpha\rangle\langle\alpha|\Big) \Bigg[\sum_{\vec{k}'} \frac{\langle \vec{k}' | U | d\rangle}{E_{\vec{k}} - E_{\vec{k}'} + i\epsilon} |\vec{k}'\rangle \Bigg] \quad . \end{aligned} \tag{50}$$

Expression (50) shows the essential features of the impurity states. The first two terms are the well-known host-metal incident wave and the pure-metal tight-binding s-scattering terms. The third term describes how already admixed s-like states (through the coefficients $a_{\vec{k}''}$) are scattered by the "reduced" impurity potential to other s-like states labeled by $\vec{k}'$. Hence, third terms are typically s-s scattering terms. The fourth term describes how host-metal s-d mixing couples scattered d states, introducing then corrections to the pure d-d tight-binding scattering states. Finally, the last term gives the direct impurity-induced s-d mixing of s-like states to the d-states.

VI. CONCLUSION

The noble- and transition-metal alloys, as the pure hosts, are described within a systematic pseudopotential approach, following Harrison's[2] scheme. In both cases one describes conduction states starting from plane waves, tight-binding sums, and imposing the orthogonality conditions between conduction states and core states. The choice of an overcomplete set of plane waves and tight-binding sums characterizes the existence of a d-band (filled or partially filled), in opposition to the non-noble, non-transition metals where only plane waves are necessary.

It turns out, from the electronic structure of the host, that the scattering wave functions for a noble-metal-based alloy are drastically different from those corresponding to a transition-metal alloy. For noble-metal hosts, the d band is completely filled, or in a more rigorous form, the states near the Fermi level are dominantly s-like. On the contrary, transition metals are characterized by a strong d-like density of states at the Fermi level, so the dominant contribution comes from the d-state tight-binding sums. These differences are reflected clearly in the nature of the scattering wave functions and the scattering equations they obey.

In the noble-metal alloys, the scattering wave functions are dominantly s-like, with corrections coming from host- and impurity-induced s-d mixing. Consequently the pseudo-wave-function obeys a Lippman-Schwinger scattering equation which is free-electron-like, the existence of d-d scattering and s-d mixing being entirely contained in the nonlocal effective impurity potential. Once the scattering equation is solved for the pseudo-wave-function, both the s-like and d-like parts of the conduction states may be derived. In transition-metal alloys, since the d-like part is dominant, one first solves a pure tight-binding impurity problem in general form,[3] the effects of host- and impurity-induced s-d mixing entering as perturbation corrections to this solution. At this point we must emphasize that for transition metals care must be taken in this perturbation approach. In fact, for strong enough perturbations and particular types of the tight-binding density of states, d-band resonances may occur, and bound states may be extracted.[3] If this is likely to occur for the impurity in question, the perturbation approach may be highly questionable if we are interested in states with energies around the resonance or the bound state. In any case, one has control over these features just looking at the behavior of the pure-tight-binding solution (more specifically looking to the d-state phase shifts) corresponding to values of the impurity potential close to the self-consistency.

APPENDIX

In order to complete the discussion of the effective impurity potential, it is useful to write down the matrix elements of U^P between plane waves, as calculated from Eq. (27):

$$
\begin{aligned}
\langle\vec{k}'|U^P|\vec{k}\rangle = {} & \langle\vec{k}'|U(1-\sum_\alpha|\alpha\rangle\langle\alpha|-\sum_d|d\rangle\langle d|)|\vec{k}\rangle+\sum_d\frac{\langle\vec{k}'|U|d\rangle\langle d|\Delta|\vec{k}\rangle}{E_d-E_{\vec{k}}} \\
& -\sum_d\langle\vec{k}'|d\rangle\langle d|U(1-\sum_\alpha|\alpha\rangle\langle\alpha|)|\vec{k}\rangle-\sum_d\frac{\langle\vec{k}'|\Delta|d\rangle\langle d|U(1-\sum_\alpha|\alpha\rangle\langle\alpha|)|\vec{k}\rangle}{E_{\vec{k}}-E_d} \\
& +\sum_d\frac{\langle\vec{k}'|U|d\rangle\langle d|U(1-\sum_\alpha|\alpha\rangle\langle\alpha|)|\vec{k}\rangle}{E_{\vec{k}}-E_d} \\
& -\sum_d\langle\vec{k}'|d\rangle\frac{\langle d|U}{1-\tilde{U}F(E_{\vec{k}})}\left(\sum_{d'}|d'\rangle\langle d'|\vec{k}\rangle+\sum_{d'}\frac{|d'\rangle\langle d'|\Delta|\vec{k}\rangle}{E_{d'}-E_{\vec{k}}}\right. \\
& \left.+\sum_{d'}\frac{|d'\rangle\langle d'|U(1-\sum_\alpha|\alpha\rangle\langle\alpha|)|\vec{k}\rangle}{E_{\vec{k}}-E_{d'}}\right)-\sum_d\frac{\langle\vec{k}'|\Delta|d\rangle}{E_d-E_{\vec{k}}}\frac{\langle d|U}{1-\tilde{U}F(E_{\vec{k}})} \\
& \times\left(\sum_{d'}|d'\rangle\langle d'|\vec{k}\rangle+\sum_{d'}\frac{|d'\rangle\langle d'|\Delta|\vec{k}\rangle}{E_{d'}-E_{\vec{k}}}+\sum_{d'}\frac{|d'\rangle\langle d'|U(1-\sum_\alpha|\alpha\rangle\langle\alpha|)|\vec{k}\rangle}{E_{\vec{k}}-E_{d'}}\right) \\
& +\sum_d\frac{\langle\vec{k}'|U|d\rangle}{E_d-E_{\vec{k}}}\frac{\langle d|U}{1-\tilde{U}F(E_{\vec{k}})}\left(\sum_{d'}|d'\rangle\langle d'|\vec{k}\rangle+\sum_{d'}\frac{|d'\rangle\langle d'|\Delta|\vec{k}\rangle}{E_{d'}-E_{\vec{k}}}\right. \\
& \left.+\sum_{d'}\frac{|d'\rangle\langle d'|U(1-\sum_\alpha|\alpha\rangle\langle\alpha|)|\vec{k}\rangle}{E_{\vec{k}}-E_{d'}}\right) .
\end{aligned}
$$

These matrix elements are important since one introduces the complete set of plane waves

$$\sum_{\vec{t}}|\vec{t}\rangle\langle\vec{t}|=1$$

in Eq. (29) in order to obtain a tractable equation for the scattering T matrix, as discussed in detail in I.

Finally, the orthogonalization procedure introduces a "reduction factor" in the "bare" impurity potential U, in the form $U(1-\sum_\alpha|\alpha\rangle\langle\alpha|)$. In the text, sometimes the "bare" potential appears as inducing s-d mixing and d-d scattering. However, the above reduced potential may be thought of as acting in these processes also because

$$
\begin{aligned}
& \langle d|U(1-\textstyle\sum_\alpha|\alpha\rangle\langle\alpha|)|d'\rangle \\
& \quad=\langle d|U|d'\rangle-\textstyle\sum_\alpha\langle d|U|\alpha\rangle\langle\alpha|d'\rangle \\
& \quad\equiv\langle d|U|d'\rangle, \\
& \langle\vec{k}|U(1-\textstyle\sum_\alpha|\alpha\rangle\langle\alpha|)|d\rangle \\
& \quad=\langle\vec{k}|U|d\rangle-\textstyle\sum_\alpha\langle\vec{k}|U|\alpha\rangle\langle\alpha|d\rangle \\
& \quad\equiv\langle\vec{k}|U|d\rangle ,
\end{aligned}
$$

since d states are automatically orthogonal to the α states. This should be compared to

$$
\begin{aligned}
& \langle\vec{k}|U(1-\textstyle\sum_\alpha|\alpha\rangle\langle\alpha|)|\vec{k}'\rangle \\
& \quad=\langle\vec{k}|U|\vec{k}'\rangle-\textstyle\sum_\alpha\langle\vec{k}|U|\alpha\rangle\langle\alpha|\vec{k}'\rangle \\
& \quad\not\equiv\langle\vec{k}|U|\vec{k}'\rangle
\end{aligned}
$$

reflecting then nonorthogonality effects.

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