

cancies is negligible both in the solid and in the liquid state.

The calculations were made explicitly for sodium. In order to obtain a simple and accurate value for other metals at low temperatures, without the problem of detailed knowledge of the solid-phase structure factor, one can use Eq. (A2). This has been done for solid sodium at 40 °K and

we find negligible error induced by using (A2) instead of (A1). Calculations for solid copper and solid silver at 40 °K using Eq. (A2) suggest a similar conclusion to that found for Na, namely, that the effect of vacancies is negligible. One may thus conclude that equilibrium concentrations of vacancies present in pure metals have no significant effect on the conduction-electron-spin-relaxation rate.

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## Pseudopotential Approach for Dilute Alloys. I. Nontransition and Non-Noble Hosts

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The electronic structure of nontransition and non-noble-metal-based alloys including charge and node effects are discussed within a pseudopotential scheme. An equivalent scattering equation for the pseudo-wave-function is obtained in terms of a nonlocal effective impurity potential. Orthogonality requirements with respect to the alloy core states are automatically fulfilled and the effective potential is shown to contain contributions from node and charge effects, whereas the scattering equation is free-electron-like. Finally the several contributions to the charge-density variations are discussed.

### I. INTRODUCTION

The impurity problem in metals involves, as is well known, two different aspects. First, one needs a precise description of the electronic structure of the host through a theoretical band calculation. Second, the self-consistent solution of the scattering problem defined by the host-metal Hamiltonian and the impurity potential must be obtained in terms of the parameters characterizing the impurity atoms. These parameters are essentially the charge difference between host and impurity atoms, and the row of the Periodic Table to which the impurity atoms belong. The latter manifests

itself through the additional closed shells introduced (or removed) locally in the host by the impurity. The above-mentioned aspects are, in general, quite difficult to handle, although the main difficulty lies in the second one through the definition of the impurity potential and its self-consistent determination. Two limiting situations have been extensively discussed in the literature<sup>1</sup>: the free-electron-like host and the tight-binding (transition-metal) host. In the first case, accurate solutions of the scattering problem using model potentials (such as the square well) show considerable success in describing situations where the important parameter associated with the impurities is the

charge difference.<sup>2</sup> On the other hand, when impurity and host belong to the same column of the Periodic Table, this picture gives quite inaccurate results<sup>2</sup>; this may be ascribed to the existence of new closed shells introduced (or removed) by the impurity potential. Transition-metal alloys have been successfully described<sup>3</sup> within the tight-binding approximation, using a phenomenological impurity potential which is determined self-consistently, but again only the cases where the charge difference effects are assumed to play the dominant role have been considered in detail.

However, several experimental results, in particular isomer-shift data,<sup>4</sup> suggest that quite systematic behavior can be observed in alloys where host and impurity belong to the same column of the Periodic Table. This "node effect" requires special care in defining the impurity problem in order to take into account the existence of these new closed shells. Several attempts have been made to formulate the alloy problem in such a way that these effects are included naturally. It seems to us that the pseudoatom approach of Ziman<sup>5</sup> is the simplest one which takes into account the details of the host and impurity atoms. However, the pseudoatom approach for alloys ignores to a certain extent the details of the scattering mechanisms, being then not directly applicable to local properties such as the isomer shift.

In the last few years, pseudopotential theory has been shown to be a very powerful tool to discuss metallic systems, and in particular it has been extended to include noble and transition metals.<sup>6</sup> It is the central point of the pseudopotential approach to include explicitly the inner-shell states (through a self-consistent atomiclike calculation), the orthogonality requirement between conduction and inner-shell states being automatically satisfied. Since the node effect involves these closed-shell states in an essential way, it seems natural to start from the pseudopotential picture to describe the changes in electronic structure due to alloying.

It is the purpose of this paper to discuss the impurity problem within a pseudopotential scheme for non-noble nontransition hosts, the case of noble and transition metals being discussed in a forthcoming paper. We adopt the following philosophy: First we introduce the scattering problem for the "true" wave functions, in terms of a self-consistent "true" impurity potential which must be determined at the end of the calculation. The next step, and this is the essence of the approach, is to obtain an *equivalent* scattering equation for a suitably defined pseudo-wave-function. This equation is obtained by defining a scattering pseudo-wave-function in such a way that the "true" scattering wave function is automatically orthogonal to the *impure-metal inner-shell states*, and requiring that when

the impurity potential is removed, the "true" wave functions reduce to their pure-metal limit. In this equivalent-equation approach, it turns out that a nonlocal effective potential replaces the otherwise local self-consistent impurity potential. When solutions of this equivalent equation are obtained, the self-consistency problem is solved through the calculation of the change in electron density obtained from the connection between pseudo- and "true"-wave-functions.

## II. FORMULATION OF THE PROBLEM

### A. Pure Metal (Main Results of the Pseudopotential Approach)

In order to introduce the notation and the ideas underlying the pseudopotential method, we begin by summarizing the main results for the pure-metal case. Let  $V(\vec{r})$  be pure-crystal self-consistent one-electron potential, assumed to be known; the one-electron states (inner and conduction) satisfy, respectively,

$$(T + V)|\alpha\rangle = E_\alpha |\alpha\rangle, \quad (1a)$$

$$(T + V)|\psi_{\vec{k}}\rangle = E_{\vec{k}} |\psi_{\vec{k}}\rangle, \quad (1b)$$

the inner-shell states  $|\alpha\rangle$  being orthogonal to the conduction states  $|\psi_{\vec{k}}\rangle$ . The pseudo-wave-functions are defined by

$$|\phi_{\vec{k}}\rangle = (1 - \sum_\alpha |\alpha\rangle \langle \alpha|) |\psi_{\vec{k}}\rangle, \quad (2)$$

so the orthogonality requirement is automatically satisfied. By substituting (2) in (1b), one verifies that the pseudo-wave-function  $|\phi_{\vec{k}}\rangle$  satisfies

$$\begin{aligned} \mathcal{H}_0 |\phi_{\vec{k}}\rangle &= [T + V + \sum_\alpha (E_{\vec{k}} - E_\alpha) |\alpha\rangle \langle \alpha|] |\phi_{\vec{k}}\rangle \\ &= E_{\vec{k}} |\phi_{\vec{k}}\rangle. \end{aligned} \quad (3)$$

Once the solutions of (3) are obtained, by substituting into (2) one gets the conduction states  $|\psi_{\vec{k}}\rangle$  to the desired degree of accuracy. One should note that equations (1a) and (3) involve a self-consistency problem in the sense that the energies  $E_\alpha$  and the wave functions  $|\alpha\rangle$  are not known *a priori*. Usually, one starts from free-ion results for  $|\alpha\rangle$  and introduces corrections until self-consistency is achieved.

### B. Definition of the Impurity Problem

An impurity entering substitutionally in an otherwise perfect normal metal introduces in the above formulation two essential modifications: (i) There appears in Eq. (1b) a self-consistent impurity one-electron potential  $U(\vec{r})$  which should be determined through a Friedel-type sum rule involving scattering states. (ii) The scattering conduction states should be orthogonal to the alloy core states.

Since these modifications define our procedure in obtaining the equivalent equation we shall discuss

them in some detail. We begin by specifying the nature of the alloy core states, introducing the following notation for them:

$$|\bar{\alpha}\rangle = |\vec{R}_\lambda, l, m, n\rangle. \quad (4)$$

In expression (4),  $\vec{R}_\lambda$  is the position vector of the  $\lambda$ th atom, the set  $\{l, m, n\}$  being the usual quantum numbers specifying atomlike functions. If the impurity is introduced at the origin ( $\vec{R}_\lambda = 0$ ), we separate the alloy core states into two groups.

(a) At the impurity site, one may have in the involved  $|\bar{\alpha}\rangle$ , quantum numbers  $\{l, m, n\}$  that do not appear in the pure metal. This is the case when the impurity and host belong to different rows of the Periodic Table, since the potential is then sufficiently attractive (or repulsive) to introduce (or remove) some new closed-shell states. However, if impurity and host belong to the same row, one has at  $\vec{R}_\lambda = 0$  the same angular quantum numbers, but probably different radial parts.

(b) For  $\vec{R}_\lambda \neq 0$  one has the same angular quantum numbers as in the host, but the radial part is probably modified. Finally, one expects that for large  $|\vec{R}_\lambda|$ , inner states are not affected too much by the impurity disturbances, so  $|\bar{\alpha}\rangle \cong |\alpha\rangle$ . It remains to discuss the nature of the scattering conduction states and the self-consistent impurity potential. The one-electron Hamiltonian for the alloy being given by

$$\mathcal{H} = T + V + U, \quad (5a)$$

we define the scattering states  $|\psi_{\vec{k}}^+\rangle$  as the outgoing solutions of the Schrödinger equation

$$(T + V + U)|\psi_{\vec{k}}^+\rangle = E_{\vec{k}}|\psi_{\vec{k}}^+\rangle. \quad (5b)$$

Besides the outgoing requirement, the states  $|\psi_{\vec{k}}^+\rangle$  must also satisfy

$$\langle \bar{\alpha} | \psi_{\vec{k}}^+ \rangle = 0 \quad \text{for all states } |\bar{\alpha}\rangle. \quad (5c)$$

From the solutions of Eq. (5b) and using the pure-metal wave functions (1b), one calculates the change in electronic density as given by

$$\Delta\rho(\vec{r}) = \sum_{\text{occ}} [|\langle \vec{r} | \psi_{\vec{k}}^+ \rangle|^2 - |\langle \vec{r} | \psi_{\vec{k}} \rangle|^2], \quad (6)$$

which, within a Hartree picture, using Poisson's theorem, defines the self-consistent impurity potential  $U(\vec{r})$  through the equation

$$q^2 U(\vec{q}) = 4\pi[Z + \Delta\rho(\vec{q})]. \quad (7)$$

In Eq. (7),  $U(\vec{q})$  and  $\Delta\rho(\vec{q})$  are the Fourier transforms of  $V(\vec{r})$  and  $\Delta\rho(\vec{r})$  and  $Z$  is the charge difference between impurity and host. Then, formally Eqs. (5b), (5c), and (7) define completely the impurity potential.

#### C. Definition of the Mixing Potential

The above formulation of the scattering states

involves the inner-shell states  $|\bar{\alpha}\rangle$  through the orthogonality condition (5c), so one needs the alloy counterpart of Eq. (1a) in order to complete the formulation. More specifically, inner-shell states enter in the problem through the orthogonality requirement and through the calculation of  $(T + V)|\bar{\alpha}\rangle$  that will be needed below in order to obtain the equivalent scattering equation for the pseudo-wave-functions. We start by defining the states  $|\bar{\alpha}\rangle$  as the solutions of an "atomiclike" Schrödinger equation

$$(T + \bar{V})|\bar{\alpha}\rangle = \bar{E}_{\bar{\alpha}}|\bar{\alpha}\rangle, \quad (8a)$$

the potential  $\bar{V}$  being defined by

$$\bar{V}(\lambda) = V + \delta V(\lambda). \quad (8b)$$

The dependence on  $\lambda$  (the position of the atom in the lattice) indicates that different solutions are expected at the impurity and next neighbors. Now we proceed to define  $\delta V(\lambda)$ , considering first the impurity site. Let  $V_i^{\text{ion}}$  be the ionic potential (as obtained from standard atomic calculations) corresponding to the  $\{l, m, n\}$  level of the impurity atom. We define the potential  $\bar{V}$  of Eqs. (8a) and (8b) as

$$\bar{V}(0) = V_i^{\text{ion}} + V_{\vec{r}}, \quad (8c)$$

where  $V_{\vec{r}}$  is a purely conduction-electron contribution to the total potential. This electronic contribution is calculated by adding to the host-metal contribution  $V - V_h^{\text{ion}}$  a correction due to impurity scattering effects, namely,  $V_{\text{screen}}$ , which is calculated from the change in electronic density  $\Delta\rho(\vec{r})$  through  $\nabla^2 V_{\text{screen}} = 4\pi\Delta\rho(\vec{r})$ . Equation (8c) can then be written as

$$\bar{V}(0) = V_i^{\text{ion}} - V_h^{\text{ion}} + V_{\text{screen}} + V. \quad (9a)$$

Comparing with equation (8b), one gets for  $\vec{R}_\lambda = 0$ ,

$$\delta V(0) = V_i^{\text{ion}} - V_h^{\text{ion}} + V_{\text{screen}}. \quad (9b)$$

For  $\vec{R}_\lambda \neq 0$  one just replaces in (8c)  $V_i^{\text{ion}}$  by  $V_h^{\text{ion}}$  which gives for  $\delta V(\lambda)$

$$\delta V(\lambda) = V_{\text{screen}}. \quad (9c)$$

In conclusion Eqs. (9b) and (9c), together with (8a) and (8b), define completely the solutions  $|\bar{\alpha}\rangle$ ,  $\bar{E}_{\bar{\alpha}}$  in this approximation. It should be emphasized that the self-consistency problem involved in pure-metal calculations still exists here through the determination of  $V_{\text{screen}}$ . Using these formulas it is possible now to calculate  $(T + V)|\bar{\alpha}\rangle$  through the following steps of Eqs. 10.

(a) Define the expectation value of  $T + V$  by  $E_{\bar{\alpha}}$ :

$$\begin{aligned} E_{\bar{\alpha}} &= \langle \bar{\alpha} | T + V | \bar{\alpha} \rangle = \langle \bar{\alpha} | T + \bar{V} | \bar{\alpha} \rangle - \langle \bar{\alpha} | \delta V | \bar{\alpha} \rangle \\ &= \bar{E}_{\bar{\alpha}} - \langle \bar{\alpha} | \delta V | \bar{\alpha} \rangle; \end{aligned} \quad (10a)$$

(b) define the mixing potential  $\Delta(\lambda)$  by

$$\Delta(\lambda)|\bar{\alpha}\rangle = \delta V(\lambda)|\bar{\alpha}\rangle - \langle \bar{\alpha} | \delta V(\lambda) | \bar{\alpha} \rangle |\bar{\alpha}\rangle. \quad (10b)$$

(c) Now one calculates

$$\begin{aligned} (T+V)|\bar{\alpha}\rangle &= (T+\bar{V})|\bar{\alpha}\rangle - \delta V(\lambda)|\bar{\alpha}\rangle \\ &= \bar{E}_{\bar{\alpha}}|\bar{\alpha}\rangle - \delta V(\lambda)|\bar{\alpha}\rangle . \end{aligned}$$

Using (10b) and (10a) one finally gets

$$(T+V)|\bar{\alpha}\rangle = E_{\bar{\alpha}}|\bar{\alpha}\rangle - \Delta(\lambda)|\bar{\alpha}\rangle . \quad (11)$$

This formula will play an essential role in the determination of the equivalent equation. It is interesting to note that the diagonal matrix elements of  $\Delta(\lambda)$  vanish identically, as can be seen from (10b).

#### D. Definition of the Pseudo-Wave-Functions and Equivalent Equation

We define the scattering pseudo-wave-functions by

$$|\psi_{\mathbf{k}}^{\pm}\rangle = (1 - \sum_{\bar{\alpha}} |\bar{\alpha}\rangle \langle \bar{\alpha}|) |\phi_{\mathbf{k}}^{\pm}\rangle , \quad (12a)$$

$|\psi_{\mathbf{k}}^{\pm}\rangle$  being the "true" scattering wave function defined in (5b). It should be emphasized that the orthogonality condition (5c) is automatically satisfied in (12a) since

$$\langle \bar{\alpha}' | \psi_{\mathbf{k}}^{\pm} \rangle = \langle \bar{\alpha}' | \phi_{\mathbf{k}}^{\pm} \rangle - \sum_{\bar{\alpha}} \langle \bar{\alpha} | \phi_{\mathbf{k}}^{\pm} \rangle \delta_{\bar{\alpha}\bar{\alpha}'} = 0 . \quad (12b)$$

The next step is to obtain the scattering equation for  $|\phi_{\mathbf{k}}^{\pm}\rangle$ ; to do that one substitutes (12a) in (5b) to get

$$\begin{aligned} (T+V)|\phi_{\mathbf{k}}^{\pm}\rangle - \sum_{\bar{\alpha}} (T+V)|\bar{\alpha}\rangle \langle \bar{\alpha} | \phi_{\mathbf{k}}^{\pm}\rangle \\ + U(1 - \sum_{\bar{\alpha}} |\bar{\alpha}\rangle \langle \bar{\alpha}|) |\phi_{\mathbf{k}}^{\pm}\rangle \\ = E_{\mathbf{k}} |\phi_{\mathbf{k}}^{\pm}\rangle - \sum_{\bar{\alpha}} E_{\bar{\alpha}} |\bar{\alpha}\rangle \langle \bar{\alpha} | \phi_{\mathbf{k}}^{\pm}\rangle . \end{aligned} \quad (13)$$

Using expression (11), the left-hand side of (13) can be written

$$\begin{aligned} (T+V)|\phi_{\mathbf{k}}^{\pm}\rangle - \sum_{\bar{\alpha}} E_{\bar{\alpha}} |\bar{\alpha}\rangle \langle \bar{\alpha} | \phi_{\mathbf{k}}^{\pm}\rangle \\ + \sum_{\bar{\alpha}} \Delta(\lambda) |\bar{\alpha}\rangle \langle \bar{\alpha} | \phi_{\mathbf{k}}^{\pm}\rangle \\ + U(1 - \sum_{\bar{\alpha}} |\bar{\alpha}\rangle \langle \bar{\alpha}|) |\phi_{\mathbf{k}}^{\pm}\rangle . \end{aligned} \quad (14a)$$

By adding and subtracting  $\sum_{\alpha} E_{\alpha} |\alpha\rangle \langle \alpha | \phi_{\mathbf{k}}^{\pm}\rangle$ ,  $|\alpha\rangle$  being the pure-metal inner-shell state, one gets

$$\begin{aligned} (T+V - \sum_{\bar{\alpha}} |E_{\bar{\alpha}}|\alpha\rangle \langle \alpha|) |\phi_{\mathbf{k}}^{\pm}\rangle + (\sum_{\alpha} E_{\alpha} |\alpha\rangle \langle \alpha| \\ - \sum_{\bar{\alpha}} E_{\bar{\alpha}} |\bar{\alpha}\rangle \langle \bar{\alpha}|) |\phi_{\mathbf{k}}^{\pm}\rangle + \sum_{\bar{\alpha}} \Delta(\lambda) |\bar{\alpha}\rangle \langle \bar{\alpha} | \phi_{\mathbf{k}}^{\pm}\rangle \\ + U(1 - \sum_{\bar{\alpha}} |\bar{\alpha}\rangle \langle \bar{\alpha}|) |\phi_{\mathbf{k}}^{\pm}\rangle . \end{aligned} \quad (14b)$$

Similarly, the right-hand side of (13) can be transformed to give

$$\begin{aligned} E_{\mathbf{k}} |\phi_{\mathbf{k}}^{\pm}\rangle - \sum_{\alpha} E_{\alpha} |\alpha\rangle \langle \alpha | \phi_{\mathbf{k}}^{\pm}\rangle + (E_{\mathbf{k}} \sum_{\alpha} |\alpha\rangle \langle \alpha| \\ - E_{\mathbf{k}} \sum_{\bar{\alpha}} |\bar{\alpha}\rangle \langle \bar{\alpha}|) |\phi_{\mathbf{k}}^{\pm}\rangle . \end{aligned} \quad (14c)$$

Equating (14b) and (14c), introducing the host-metal pseudo-Hamiltonian

$$\mathfrak{H}_{\mathbf{k}}^{\phi} = T + V + \sum_{\alpha} (E_{\mathbf{k}} - E_{\alpha}) |\alpha\rangle \langle \alpha| ,$$

and defining the effective nonlocal impurity potential  $U^{\phi}$  by

$$\begin{aligned} U^{\phi} = U(1 - \sum_{\bar{\alpha}} |\bar{\alpha}\rangle \langle \bar{\alpha}|) \\ + (\sum_{\alpha} E_{\alpha} |\alpha\rangle \langle \alpha| - \sum_{\bar{\alpha}} E_{\bar{\alpha}} |\bar{\alpha}\rangle \langle \bar{\alpha}|) \\ - E_{\mathbf{k}} (\sum_{\alpha} |\alpha\rangle \langle \alpha| - \sum_{\bar{\alpha}} |\bar{\alpha}\rangle \langle \bar{\alpha}|) \\ + \sum_{\bar{\alpha}} \Delta(\lambda) |\bar{\alpha}\rangle \langle \bar{\alpha}| , \end{aligned} \quad (14d)$$

one gets

$$(E_{\mathbf{k}} - \mathfrak{H}_{\mathbf{k}}^{\phi}) |\phi_{\mathbf{k}}^{\pm}\rangle = U^{\phi} |\phi_{\mathbf{k}}^{\pm}\rangle . \quad (15a)$$

This is the equivalent equation for the scattered pseudo-wave-function, which is the alloy counterpart of the pure-metal pseudo-Schrödinger-equation (3). It remains however to incorporate the condition

$$\lim |\phi_{\mathbf{k}}^{\pm}\rangle = |\phi_{\mathbf{k}}\rangle \text{ as } U \rightarrow 0 \text{ and } |\bar{\alpha}\rangle \rightarrow |\alpha\rangle , \quad (15b)$$

where  $|\phi_{\mathbf{k}}\rangle$  is the solution of Eq. (3) and the outgoing behavior of the scattered wave functions. These two conditions are fulfilled if instead of (15a) one writes

$$|\phi_{\mathbf{k}}^{\pm}\rangle = |\phi_{\mathbf{k}}\rangle + (E_{\mathbf{k}} - \mathfrak{H}_{\mathbf{k}}^{\phi} + i\epsilon)^{-1} U^{\phi} |\phi_{\mathbf{k}}^{\pm}\rangle . \quad (16)$$

Equation (16) is the Lippman-Schwinger equation for pseudo-wave-functions. At this point it is worthwhile to rewrite (16) in coordinate space and to introduce the transition amplitudes. Following Harrison<sup>6</sup> it will be assumed that the pure-metal inner states  $|\alpha\rangle$  are accurate enough to allow the representation of  $|\phi_{\mathbf{k}}\rangle$  by a single plane wave. Although not essential, this assumption simplifies the following calculations. Multiplying Eq. (16) by  $|\bar{\mathbf{r}}\rangle$ , defining the effective potential in coordinate space as  $U^{\phi}(\bar{\mathbf{r}}_1, \bar{\mathbf{r}}_2) = \langle \bar{\mathbf{r}}_1 | U^{\phi} | \bar{\mathbf{r}}_2 \rangle$ , and remembering that plane waves form a complete set ( $\sum_{\bar{\mathbf{t}}} |\bar{\mathbf{t}}\rangle \langle \bar{\mathbf{t}}| = 1$ ), one obtains

$$\begin{aligned} \phi_{\mathbf{k}}^{\pm}(\bar{\mathbf{r}}) = e^{i\bar{\mathbf{k}} \cdot \bar{\mathbf{r}}} + \iint d\bar{\mathbf{r}}_1 d\bar{\mathbf{r}}_2 \int \frac{d\bar{\mathbf{t}}}{(2\pi)^3} \frac{e^{i\bar{\mathbf{t}} \cdot (\bar{\mathbf{r}} - \bar{\mathbf{r}}_1)}}{E_{\bar{\mathbf{k}}} - E_{\bar{\mathbf{t}}} + i\epsilon} \\ \times U^{\phi}(\bar{\mathbf{r}}_1, \bar{\mathbf{r}}_2) \phi_{\mathbf{k}}^{\pm}(\bar{\mathbf{r}}_2) . \end{aligned} \quad (17)$$

The transition amplitude is defined in the usual way

$$\begin{aligned} f(\bar{\mathbf{k}}', \bar{\mathbf{k}}) = (-1/4\pi) \iint d\bar{\mathbf{r}}_1 d\bar{\mathbf{r}}_2 e^{-i\bar{\mathbf{k}}' \cdot \bar{\mathbf{r}}_1} \\ \times U^{\phi}(\bar{\mathbf{r}}_1, \bar{\mathbf{r}}_2) \phi_{\mathbf{k}}^{\pm}(\bar{\mathbf{r}}_2) . \end{aligned} \quad (18)$$

In terms of the transition amplitudes, the scattered pseudo-wave-functions read

$$\phi_{\mathbf{k}}^{\pm}(\bar{\mathbf{r}}) = e^{i\bar{\mathbf{k}} \cdot \bar{\mathbf{r}}} - 4\pi \int \frac{d\bar{\mathbf{t}}}{(2\pi)^3} \frac{f(\bar{\mathbf{t}}, \bar{\mathbf{k}}) e^{i\bar{\mathbf{t}} \cdot \bar{\mathbf{r}}}}{E_{\bar{\mathbf{k}}} - E_{\bar{\mathbf{t}}} + i\epsilon} , \quad (19)$$

showing that these transition amplitudes specify completely the scattered function. It remains to obtain the integral equation from which one calcu-

lates the amplitudes  $f(\vec{k}', \vec{k})$ . To do that it is useful to define the  $T$  matrix, whose matrix elements between plane-wave states give directly the transition amplitudes. The  $T$  matrix is defined as

$$T|\vec{k}\rangle = U^p |\phi_{\vec{k}}^+\rangle . \quad (20)$$

From this definition, and comparing with (18), the connection between  $\langle \vec{k}' | T | \vec{k} \rangle$  and  $f(\vec{k}', \vec{k})$  turns out to be

$$\begin{aligned} T(\vec{k}', \vec{k}) &= \langle \vec{k}' | T | \vec{k} \rangle = \langle \vec{k}' | U^p | \phi_{\vec{k}}^+ \rangle \\ &= \int \int d\vec{r}_1 d\vec{r}_2 \langle \vec{k}' | \vec{r}_1 \rangle U^p(\vec{r}_1, \vec{r}_2) \phi_{\vec{k}}^+(\vec{r}_2) \\ &= -4\pi f(\vec{k}', \vec{k}) . \end{aligned} \quad (21)$$

The integral equation for the  $T$ -matrix elements is easily derived from the Lippman-Schwinger equation (16). Applying the operator  $U^p$  to (16) one has

$$\begin{aligned} \langle \vec{k}' | U^p | \phi_{\vec{k}}^+ \rangle &= \langle \vec{k}' | U^p | \vec{k} \rangle \\ &+ \langle \vec{k}' | U^p (E_{\vec{k}} - \mathcal{H}_0^p + i\epsilon)^{-1} U^p | \phi_{\vec{k}}^+ \rangle . \end{aligned} \quad (22)$$

Using the definition (20) and  $\sum_{\vec{t}} |\vec{t}\rangle \langle \vec{t}| = 1$ , and defining  $U^p(\vec{k}', \vec{k}) = \langle \vec{k}' | U^p | \vec{k} \rangle$ , one obtains

$$\begin{aligned} T(\vec{k}', \vec{k}) &= U^p(\vec{k}', \vec{k}) \\ &+ \int \frac{d\vec{t}}{(2\pi)^3} U^p(\vec{k}', \vec{t}) \frac{1}{E_{\vec{k}} - E_{\vec{t}} + i\epsilon} T(\vec{t}, \vec{k}) . \end{aligned} \quad (23)$$

These equations must be solved either for model potentials (giving exact solutions) or numerically for the effective potential defined in (14d). In Appendix B, Eq. (23) is solved exactly for a model potential.

When solutions of (23) are available, one obtains through the definition (12a) the "true" scattering wave functions. The formal expression for  $|\psi_{\vec{k}}^+\rangle$  is more easily obtained by transforming (19) back to the ket notation

$$|\phi_{\vec{k}}^+\rangle = |\vec{k}\rangle - 4\pi \int \frac{d\vec{t}}{(2\pi)^3} \frac{f(\vec{t}, \vec{k}) |\vec{t}\rangle}{E_{\vec{k}} - E_{\vec{t}} + i\epsilon} . \quad (24)$$

Substituting (24) into definition (12a) one gets

$$\begin{aligned} |\psi_{\vec{k}}^+\rangle &= |\vec{k}\rangle - \sum_{\vec{\alpha}} \langle \vec{\alpha} | \vec{k} \rangle |\vec{\alpha}\rangle - 4\pi \int \frac{d\vec{t}}{(2\pi)^3} \frac{f(\vec{t}, \vec{k}) |\vec{t}\rangle}{E_{\vec{k}} - E_{\vec{t}} + i\epsilon} \\ &+ 4\pi \sum_{\vec{\alpha}} |\vec{\alpha}\rangle \int \frac{d\vec{t}}{(2\pi)^3} \frac{f(\vec{t}, \vec{k}) \langle \vec{\alpha} | \vec{t} \rangle}{E_{\vec{k}} - E_{\vec{t}} + i\epsilon} . \end{aligned} \quad (25)$$

Finally, introducing the notation  $\psi_{\vec{\alpha}}(\vec{r}) = \langle \vec{r} | \vec{\alpha} \rangle$  for the alloy inner-shell states, one gets

$$\begin{aligned} \psi_{\vec{k}}^+(\vec{r}) &= e^{i\vec{k} \cdot \vec{r}} - \sum_{\vec{\alpha}} \langle \vec{\alpha} | \vec{k} \rangle \psi_{\vec{\alpha}}(\vec{r}) \\ &- 4\pi \int \frac{d\vec{t}}{(2\pi)^3} \frac{f(\vec{t}, \vec{k}) e^{i\vec{t} \cdot \vec{r}}}{E_{\vec{k}} - E_{\vec{t}} + i\epsilon} \\ &+ 4\pi \sum_{\vec{\alpha}} \psi_{\vec{\alpha}}(\vec{r}) \int \frac{d\vec{t}}{(2\pi)^3} \frac{f(\vec{t}, \vec{k}) \langle \vec{\alpha} | \vec{t} \rangle}{E_{\vec{k}} - E_{\vec{t}} + i\epsilon} . \end{aligned} \quad (26)$$

From (26) it is clear that

$$\begin{aligned} \lim \psi_{\vec{k}}^+(\vec{r}) &= e^{i\vec{k} \cdot \vec{r}} - \sum_{\vec{\alpha}} \langle \vec{\alpha} | \vec{k} \rangle \psi_{\vec{\alpha}}(\vec{r}) \\ &\text{as } U \rightarrow 0, \quad |\vec{\alpha}\rangle = |\alpha\rangle , \end{aligned}$$

which is the true wave function for the pure metal.

#### E. Change in Electronic Density and Self-Consistency Problem

The solution of the scattering problem defined by Eq. (23) involves the self-consistent impurity potential  $U$ . As we have discussed above [cf. Eqs. (6) and (7)], for a given charge difference  $Z$ , the potential  $U$  is defined through Eq. (7) self-consistently in terms of the  $U$  dependence of the charge-density variation defined in (6). Now we obtain an explicit expression for  $\Delta\rho(\vec{r})$ , starting from the solution (26) of the scattering problem, which depends explicitly on  $U$  only through the transition probabilities  $f(\vec{k}, \vec{k}')$ . This calculation (cf. Appendix A for details) shows that the change in electronic density is the sum of these terms:

$$\begin{aligned} \Delta\rho(\vec{r}) &= \sum_{\vec{k}_{\text{occ}}} \Delta\rho_{\vec{k}}(\vec{r}) = \Delta\rho^{\text{orth}}(\vec{r}) + \Delta\rho^{\text{free}}(\vec{r}) \\ &+ \Delta\rho^{\text{free} + \text{orth}}(\vec{r}) , \end{aligned} \quad (27)$$

where these contributions are defined as follows.

First we have

$$\begin{aligned} \Delta\rho^{\text{orth}}(\vec{r}) &= 2 \text{Re} \sum_{\vec{k}_{\text{occ}}} \left( e^{-i\vec{k} \cdot \vec{r}} \sum_{\vec{\alpha}} \psi_{\vec{\alpha}}(\vec{r}) \langle \vec{\alpha} | \vec{k} \rangle \right. \\ &- \sum_{\vec{\alpha}} \psi_{\vec{\alpha}}(\vec{r}) \langle \vec{\alpha} | \vec{k} \rangle \left. \right) + \sum_{\vec{k}_{\text{occ}}} \left( \sum_{\vec{\alpha}, \vec{\alpha}'} \psi_{\vec{\alpha}}(\vec{r}) \psi_{\vec{\alpha}'}^*(\vec{r}) \right. \\ &\times (\vec{r}) \langle \vec{\alpha} | \vec{k} \rangle \langle \vec{k} | \vec{\alpha}' \rangle \\ &- \sum_{\alpha, \alpha'} \psi_{\alpha}(\vec{r}) \psi_{\alpha'}(\vec{r}) \langle \alpha | \vec{k} \rangle \langle \vec{k} | \alpha' \rangle \left. \right) . \end{aligned} \quad (28)$$

One notes that in the contribution  $\Delta\rho^{\text{orth}}(\vec{r})$  the scattering amplitudes are absent and only inner-shell differences are present. This can be then interpreted as the "orthogonalization charge" and gives a measure of the effect of the orthogonality condition in introducing (or removing) new closed shells. This effect is expected to be small when impurity and host belong to the same row of the Periodic Table.

Second we define

$$\Delta\rho^{\text{free}}(\vec{r}) = \sum_{\vec{k}_{\text{occ}}} \{-2 \text{Re} [e^{-i\vec{k} \cdot \vec{r}} F(\vec{k}, \vec{r})] + |F(\vec{k}, \vec{r})|^2\} ,$$

where

$$F(\vec{k}, \vec{r}) = 4\pi \int \frac{d\vec{t}}{(2\pi)^3} \frac{f(\vec{k}, \vec{t}) e^{i\vec{t} \cdot \vec{r}}}{E_{\vec{k}} - E_{\vec{t}} + i\epsilon} . \quad (29)$$

This "free-electron" contribution corresponds formally to the change in electronic density produced by the scattering of free electrons by a poten-

tial which is defined through the transition amplitudes  $f(\vec{k}, \vec{k}')$ .

Finally, there remain the "interference terms"

$$\begin{aligned} \Delta\rho^{\text{free-orth}}(\vec{r}) = & 2 \operatorname{Re} \sum_{\vec{k}_{\text{occ}}} \left( \sum_{\vec{\alpha}} \psi_{\vec{\alpha}}(\vec{r}) e^{-i\vec{k} \cdot \vec{r}} \langle \vec{\alpha} | F(\vec{k}) \rangle \right) + 2 \operatorname{Re} \sum_{\vec{k}_{\text{occ}}} \left( \sum_{\vec{\alpha}} \langle \vec{k} | \vec{\alpha} \rangle \psi_{\vec{\alpha}}^*(\vec{r}) F(\vec{k}, \vec{r}) \right) \\ & - 2 \operatorname{Re} \sum_{\vec{k}_{\text{occ}}} \left( \sum_{\vec{\alpha}} \psi_{\vec{\alpha}}(\vec{r}) F^*(\vec{k}, \vec{r}) \langle \vec{\alpha} | F(\vec{k}) \rangle \right) - 2 \operatorname{Re} \sum_{\vec{k}_{\text{occ}}} \left( \sum_{\vec{\alpha}, \vec{\alpha}'} \langle \vec{k} | \vec{\alpha} \rangle \psi_{\vec{\alpha}}^*(\vec{r}) \psi_{\vec{\alpha}'}(\vec{r}) \langle \vec{\alpha}' | F(\vec{k}) \rangle \right) \\ & + \sum_{\vec{k}_{\text{occ}}} \left( \sum_{\vec{\alpha}, \vec{\alpha}'} \psi_{\vec{\alpha}}(\vec{r}) \psi_{\vec{\alpha}'}^*(\vec{r}) \langle \vec{\alpha} | F(\vec{k}) \rangle \langle F(\vec{k}) | \vec{\alpha}' \rangle \right). \quad (30) \end{aligned}$$

The self-consistency problem is solved through Eqs. (6) and (7).

### III. DISCUSSION

The equivalent problem described by Eqs. (14d) and (16) provides a very clear picture of node and charge effects. As was discussed in the Introduction, the usual description of non-noble non-transition-metal-based alloys corresponds to solving the scattering problem defined by a free-electron gas and a potential well, whose depth is adjusted by the Friedel sum rule. In the picture developed here one still has a "free-electron-like" scattering equation, but band effects are incorporated in the effective potential  $U^p$  defined by (14b) and in the energy  $E_{\vec{k}}$ . It is also possible to separate the contributions from the node effects and the pure charge effects, as will be discussed now. The effective impurity potential (14d) contains two different terms, which are nonlocal, and correspond to the following.

(i) The mixing potential

$$\begin{aligned} \sum_{\vec{\alpha}} \Delta(\lambda) |\vec{\alpha}\rangle \langle \vec{\alpha}| + (\sum_{\alpha} E_{\alpha} |\alpha\rangle \langle \alpha| \\ - \sum_{\vec{\alpha}} E_{\vec{\alpha}} |\vec{\alpha}\rangle \langle \vec{\alpha}|) - E_{\vec{k}} (\sum_{\alpha} |\alpha\rangle \langle \alpha| - \sum_{\vec{\alpha}} |\vec{\alpha}\rangle \langle \vec{\alpha}|) \end{aligned}$$

describes how the orthogonalization requirement affects the nature of the conduction states. In fact, when acting on plane waves, this potential couples to the spherical harmonics corresponding to the new core states introduced by the impurity. One may therefore have enhanced  $p$ - or  $d$ -wave scattering according to the existence of new  $p$  or  $d$  closed shells. It should be noted that when impurity and host lie in the same row of the Periodic Table (charge effects dominant) these terms may be neglected since  $E_{\alpha} \cong E_{\vec{\alpha}}$  and  $|\vec{\alpha}\rangle \cong |\alpha\rangle$ .

(ii) The "charge" and reaction potential  $U(1 - \sum_{\vec{\alpha}} |\vec{\alpha}\rangle \langle \vec{\alpha}|)$  is just the self-consistent impurity potential  $U$  reduced by the factor  $(1 - \sum_{\vec{\alpha}} |\vec{\alpha}\rangle \langle \vec{\alpha}|)$ , the reduction being introduced by the orthogonalization. The meaning of "reaction" potential can be understood by considering the case of impurity and host belonging to the same column of the Periodic Table. In this situation the charge difference  $Z$  is

$\Delta\rho^{\text{orth+free}}(\vec{r})$  which describe how orthogonality requirements affect the scattered free-electron waves. These terms are given by

zero, and the existence of new closed shells produces a nonvanishing value of the mixing potential. If this were the only contribution to  $U^p$ , this would displace a net charge  $Z$  different from zero, thus violating the charge neutrality requirement. The role of  $U(1 - \sum_{\vec{\alpha}} |\vec{\alpha}\rangle \langle \vec{\alpha}|)$  is then to compensate these charges, and corresponds to a rearrangement of the electron gas to compensate the orthogonalization hole. Then for the  $Z = 0$  case, the potential  $U(1 - \sum_{\vec{\alpha}} |\vec{\alpha}\rangle \langle \vec{\alpha}|)$  has the meaning of a reaction potential.

For the general case,  $U$  contains both the charge and reaction components.

### APPENDIX A: CALCULATION OF THE CHANGE IN ELECTRONIC DENSITY

In this Appendix we evaluate  $\Delta\rho(\vec{r})$ , expression (6), explicitly for  $\psi_{\vec{k}}(\vec{r})$  and  $\psi_{\vec{k}}^*(\vec{r})$  given, respectively, by expressions (2) and (26). The pure-metal electronic density associated to wave vector  $\vec{k}$  is given by

$$\begin{aligned} |\psi_{\vec{k}}(\vec{r})|^2 = & [e^{-i\vec{k} \cdot \vec{r}} - \sum_{\alpha} \psi_{\alpha}^*(\vec{r}) \langle \vec{k} | \alpha \rangle] \\ & \times [e^{i\vec{k} \cdot \vec{r}} - \sum_{\alpha} \psi_{\alpha}(\vec{r}) \langle \alpha | \vec{k} \rangle], \\ |\psi_{\vec{k}}^*(\vec{r})|^2 = & 1 - 2 \operatorname{Re} \sum_{\alpha} e^{-i\vec{k} \cdot \vec{r}} \psi_{\alpha}(\vec{r}) \langle \alpha | \vec{k} \rangle \quad (A1) \\ & + \sum_{\alpha, \alpha'} \psi_{\alpha}^*(\vec{r}) \psi_{\alpha'}(\vec{r}) \langle \vec{k} | \alpha \rangle \langle \alpha' | \vec{k} \rangle. \end{aligned}$$

The alloy electronic density is then calculated from

$$\begin{aligned} |\psi_{\vec{k}}^*(\vec{r})|^2 = & \left| e^{i\vec{k} \cdot \vec{r}} - \sum_{\vec{\alpha}} \langle \vec{\alpha} | \vec{k} \rangle \psi_{\vec{\alpha}}(\vec{r}) \right. \\ & - 4\pi \int \frac{d\vec{t}}{(2\pi)^3} \frac{f(\vec{t}, \vec{k}) e^{i\vec{t} \cdot \vec{r}}}{E_{\vec{k}} - E_{\vec{t}} + i\epsilon} \\ & \left. + 4\pi \sum_{\vec{\alpha}} \psi_{\vec{\alpha}}^*(\vec{r}) \int \frac{d\vec{t}}{(2\pi)^3} \frac{f(\vec{t}, \vec{k}) \langle \vec{\alpha} | \vec{t} \rangle}{E_{\vec{k}} - E_{\vec{t}} + i\epsilon} \right|^2. \quad (A2) \end{aligned}$$

From (A2) one sees that three types of terms occur. First one has terms involving only orthogonality effects through the inner-shell functions

$\psi_{\bar{\alpha}}(\vec{r})$ ; secondly one has terms involving the transition probabilities, and these are "free-electron-like"; finally one has interference terms character-

izing the orthogonality of scattered free-electron waves to inner-shell states. Now we evaluate explicitly (A2) collecting the above-mentioned terms:

$$\begin{aligned}
|\psi_{\vec{k}}^{\dagger}(\vec{r})|^2 &= 1 - 2 \operatorname{Re} \sum_{\bar{\alpha}} \langle \bar{\alpha} | \vec{k} \rangle \psi_{\bar{\alpha}}(\vec{r}) e^{-i\vec{k} \cdot \vec{r}} \\
&+ \sum_{\bar{\alpha}, \bar{\alpha}'} \langle \bar{\alpha} | \vec{k} \rangle \langle \vec{k} | \bar{\alpha}' \rangle \psi_{\bar{\alpha}}(\vec{r}) \psi_{\bar{\alpha}'}^*(\vec{r}) - 8\pi \operatorname{Re} \left( e^{-i\vec{k} \cdot \vec{r}} \int \frac{d\vec{t}}{(2\pi)^3} \frac{f(\vec{t}, \vec{k}) e^{i\vec{t} \cdot \vec{r}}}{E_{\vec{k}} - E_{\vec{t}} + i\epsilon} \right) \\
&+ (4\pi)^2 \left| \int \frac{d\vec{t}}{(2\pi)^3} \frac{f(\vec{t}, \vec{k}) e^{i\vec{t} \cdot \vec{r}}}{E_{\vec{k}} - E_{\vec{t}} + i\epsilon} \right|^2 + 8\pi \operatorname{Re} \sum_{\bar{\alpha}} \psi_{\bar{\alpha}}(\vec{r}) e^{-i\vec{k} \cdot \vec{r}} \int \frac{d\vec{t}}{(2\pi)^3} \frac{f(\vec{t}, \vec{k}) \langle \bar{\alpha} | \vec{k} \rangle}{E_{\vec{k}} - E_{\vec{t}} + i\epsilon} \\
&+ 8\pi \operatorname{Re} \sum_{\bar{\alpha}} \langle \vec{k} | \bar{\alpha} \rangle \psi_{\bar{\alpha}}^*(\vec{r}) \int \frac{d\vec{t}}{(2\pi)^3} \frac{f(\vec{t}, \vec{k}) e^{i\vec{t} \cdot \vec{r}}}{E_{\vec{k}} - E_{\vec{t}} + i\epsilon} \\
&- 8\pi \operatorname{Re} \sum_{\bar{\alpha}, \bar{\alpha}'} \langle \vec{k} | \bar{\alpha} \rangle \psi_{\bar{\alpha}}^*(\vec{r}) \psi_{\bar{\alpha}'}(\vec{r}) \int \frac{d\vec{t}}{(2\pi)^3} \frac{f(\vec{t}, \vec{k}) \langle \bar{\alpha}' | \vec{t} \rangle}{E_{\vec{k}} - E_{\vec{t}} + i\epsilon} \\
&+ (4\pi)^2 \sum_{\bar{\alpha}, \bar{\alpha}'} \psi_{\bar{\alpha}}(\vec{r}) \psi_{\bar{\alpha}'}^*(\vec{r}) \int \frac{d\vec{t}}{(2\pi)^3} \frac{f(\vec{t}, \vec{k}) \langle \bar{\alpha} | \vec{t} \rangle}{E_{\vec{k}} - E_{\vec{t}} + i\epsilon} \int \frac{d\vec{t}'}{(2\pi)^3} \frac{f(\vec{t}', \vec{k}) \langle \vec{t}' | \bar{\alpha}' \rangle}{E_{\vec{k}} - E_{\vec{t}'} - i\epsilon} \\
&- 2(4\pi)^2 \operatorname{Re} \sum_{\bar{\alpha}} \psi_{\bar{\alpha}}(\vec{r}) \int \frac{d\vec{t}}{(2\pi)^3} \frac{f(\vec{t}, \vec{k}) \langle \bar{\alpha} | \vec{t} \rangle}{E_{\vec{k}} - E_{\vec{t}} + i\epsilon} \int \frac{d\vec{t}'}{(2\pi)^3} \frac{f^*(\vec{t}', \vec{k}) e^{-i\vec{t}' \cdot \vec{r}}}{E_{\vec{k}} - E_{\vec{t}'} - i\epsilon} . \quad (\text{A3})
\end{aligned}$$

In order to simplify the notation we introduce the following definitions:

$$F(\vec{k}, \vec{r}) = 4\pi \int \frac{d\vec{t}}{(2\pi)^3} \frac{f(\vec{t}, \vec{k}) e^{i\vec{t} \cdot \vec{r}}}{E_{\vec{k}} - E_{\vec{t}} + i\epsilon} , \quad (\text{A4a})$$

$$|F(\vec{k})\rangle = 4\pi \int \frac{d\vec{t}}{(2\pi)^3} \frac{f(\vec{t}, \vec{k}) |\vec{t}\rangle}{E_{\vec{k}} - E_{\vec{t}} + i\epsilon} . \quad (\text{A4b})$$

It follows then from (A1) and (A3) that the change in electronic density  $\Delta\rho_{\vec{k}}(\vec{r})$  is the sum of three contributions:

$$\begin{aligned}
\Delta\rho_{\vec{k}}(\vec{r}) &= |\psi_{\vec{k}}^{\dagger}(\vec{r})|^2 - |\psi_{\vec{k}}(\vec{r})|^2 \\
&= \Delta\rho_{\vec{k}}^{\text{orth}}(\vec{r}) + \Delta\rho_{\vec{k}}^{\text{free}}(\vec{r}) \\
&\quad + \Delta\rho_{\vec{k}}^{\text{free+orth}}(\vec{r}) , \quad (\text{A5a})
\end{aligned}$$

where

$$\begin{aligned}
\Delta\rho_{\vec{k}}^{\text{orth}}(\vec{r}) &= 2 \operatorname{Re} \left[ e^{-i\vec{k} \cdot \vec{r}} \left( \sum_{\bar{\alpha}} \psi_{\bar{\alpha}}(\vec{r}) \langle \bar{\alpha} | \vec{k} \rangle \right. \right. \\
&\quad \left. \left. - \sum_{\bar{\alpha}} \psi_{\bar{\alpha}}(\vec{r}) \langle \bar{\alpha} | \vec{k} \rangle \right) \right] \\
&+ \sum_{\bar{\alpha}, \bar{\alpha}'} \psi_{\bar{\alpha}}(\vec{r}) \psi_{\bar{\alpha}'}^*(\vec{r}) \langle \bar{\alpha} | \vec{k} \rangle \langle \vec{k} | \bar{\alpha}' \rangle \\
&- \sum_{\bar{\alpha}, \bar{\alpha}'} \psi_{\bar{\alpha}}(\vec{r}) \psi_{\bar{\alpha}'}^*(\vec{r}) \langle \bar{\alpha} | \vec{k} \rangle \langle \vec{k} | \bar{\alpha}' \rangle , \quad (\text{A5b})
\end{aligned}$$

$$\Delta\rho_{\vec{k}}^{\text{free}}(\vec{r}) = 2 \operatorname{Re} [ e^{-i\vec{k} \cdot \vec{r}} F(\vec{k}, \vec{r}) ] + |F(\vec{k}, \vec{r})|^2 , \quad (\text{A5c})$$

$$\begin{aligned}
\Delta\rho_{\vec{k}}^{\text{free+orth}}(\vec{r}) &= 2 \operatorname{Re} \left( \sum_{\bar{\alpha}} \psi_{\bar{\alpha}}(\vec{r}) e^{-i\vec{k} \cdot \vec{r}} \langle \bar{\alpha} | F(\vec{k}) \rangle \right) \\
&+ 2 \operatorname{Re} \left( \sum_{\bar{\alpha}} \langle \vec{k} | \bar{\alpha} \rangle \psi_{\bar{\alpha}}^*(\vec{r}) F(\vec{k}, \vec{r}) \right)
\end{aligned}$$

$$\begin{aligned}
&- 2 \operatorname{Re} \left( \sum_{\bar{\alpha}} \psi_{\bar{\alpha}}(\vec{r}) F^*(\vec{k}, \vec{r}) \langle \bar{\alpha} | F(\vec{k}) \rangle \right) \\
&- 2 \operatorname{Re} \left( \sum_{\bar{\alpha}, \bar{\alpha}'} \langle \vec{k} | \bar{\alpha} \rangle \psi_{\bar{\alpha}}^*(\vec{r}) \psi_{\bar{\alpha}'}(\vec{r}) \langle \bar{\alpha}' | F(\vec{k}) \rangle \right) \\
&+ \sum_{\bar{\alpha}, \bar{\alpha}'} \psi_{\bar{\alpha}}(\vec{r}) \psi_{\bar{\alpha}'}^*(\vec{r}) \langle \bar{\alpha} | F(\vec{k}) \rangle \langle F(\vec{k}) | \bar{\alpha}' \rangle . \quad (\text{A5d})
\end{aligned}$$

#### APPENDIX B: SOLUTION OF THE $T$ -MATRIX EQUATION FOR MODEL POTENTIALS

The  $T$ -matrix equation (23) is now solved for an approximate version of the effective potential  $U^p$  defined in Eq. (14d). This approximate potential is called a "model potential." The approximation consists in replacing the first term of (14d) by a *separable* nonlocal potential, namely,

$$U(1 - \sum_{\bar{\alpha}} |\bar{\alpha}\rangle \langle \bar{\alpha}|) \cong \sum_{\bar{\alpha}} A_{\bar{\alpha}} |\bar{\alpha}\rangle \langle \bar{\alpha}| , \quad (\text{B1})$$

where  $A_{\bar{\alpha}}$  will be chosen in such a way that the self-consistency rule (6) is satisfied through Eq. (27). Since all the terms involved in (14d) are now of the form (B1), we consider the following model potential:

$$U^p = \sum_{\Gamma} A_{\Gamma} |\Gamma\rangle \langle \Gamma| , \quad (\text{B2})$$

$|\Gamma\rangle$  being "atomiclike" states.

Now we introduce the following notation:

$$\langle \vec{k} | \Gamma \rangle = v_{\Gamma}(\vec{k}) , \quad (\text{B3a})$$

$$\langle \Gamma | \vec{k}' \rangle = v_{\Gamma}^*(\vec{k}') , \quad (\text{B3b})$$

$$U^p(\vec{k}', \vec{k}) = \langle \vec{k}' | U^p | \vec{k} \rangle = \sum_{\Gamma} A_{\Gamma} v_{\Gamma}(\vec{k}') v_{\Gamma}^*(\vec{k}) . \quad (\text{B3c})$$

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

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

Introduce the auxiliary notation

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

which gives for (B4)

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

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

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

which can be written as

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

where

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

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

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<sup>1</sup> (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,<sup>2</sup> and the main point of the approach is to realize that tight-binding sums