PSEUDO POTENTIAL APPROACH OF NOBLE AND TRANSITION METAL

BASED ALLOYS (CHARGE EFFECTS)

by

X. A. da Silva, A. A. Gomes and J. Danon

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INTRODUCTION

In a previous work [1] (referred as I) the case of normal metal alloys was discussed within a pseudo-potential approach, paying special attention to node effects. In that case, the electronic strucutre of the host was characterized by a broad conduction band, and a set of atomic-like sharp bands defining inner shell states (fig. 1). The node effects discussed there involved essentially orthogonalization effects introduced by the extra atomic states associated to 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 neighbourhood of the Fermi level (cf. fig. 2 and 3).

These d-states introduce further difficulties in the discussion of the alloy electronic structure even in the absence of node effects, so in this work we restrict ourselves to the simplest case of dominant charge effect. The pseudo-potential 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

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 [2]. In this way in the limit of zero impurity perturbation one recovers Harrison's pseudo potential description of the transition host metal.

FORMULATION OF THE IMPURITY PROBLEM FOR THE NOBLE METAL CASE

We start defining the alloy wave function, assuming from the begining that node effects may be disregarded. The case of impurity and host belonging to different lines of the periodic table may be handled in similar lines to those developped previously (I); the only difference respect to normal metals is that d-states must be included in considering the node effects. We start defining the "true" scattered wave function $|\psi_k^+>$, solution of

$$(T+V+U)|\psi_k^+> = E_k| \psi_k^+ > \qquad (1)$$

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)

$$<\alpha|\psi_k^+> = 0 \text{ for all states } |\alpha> \qquad (2)$$

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

$$\lim_{U \to 0} |\psi_k^+> = |\psi_k> \qquad (3)$$

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

A very convenient way of writting $|\psi_k^+ >$ is provided [2] by an expansion in terms of an overcomplete set of plane waves and tight-binding d-states. In doing so, one automatically fulfills condition (i) since for

where in the absence of node effects we used:

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

Now equation (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 [1]:

$$<d|T+V|\phi_k^+> = E_d<d|\phi_k^+> - <d|\Delta|\phi_k^+> \tag{8-a}$$

which follows from:

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

where

$$E_d = <d|T+V|d> \tag{8-c}$$

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

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

and

$$\Sigma_{d'} \,\alpha_{d'} <d|\Delta|d'> = 0 \tag{8-e}$$

for any c-numbers $\{\alpha_{d'}\}$, using the tight-binding approximations.

Performing the calculation through these steps one gets:

$$<d|T+V|\phi_k^+> + \Sigma_{d'} \,a_{d'}^{(+)}<d|T+V|d'> + <d|U(1-\Sigma_\alpha|\alpha><\alpha|)|\phi_k^+>$$

$$+ \Sigma_{d'} \,a_{d'}^{(+)}<d|U|d'> = E_k<d|\phi_k^+> + E_k \,a_d^{(+)} \tag{9}$$

where use was made of $<\alpha|d> = 0$ for any $|\alpha>$ and $|d>$. Using equations (8-a), (8-d) and (8-e) one rewrites (9) as:

$$E_d <d|\phi_k^+> - <d|\Delta|\phi_k^+> + E_d \,a_d^{(+)} + <d|U(1-\Sigma_\alpha|\alpha><\alpha|\phi_k^+>$$

$$+ \Sigma_{d'} \,a_{d'}^{(+)}<d|U|d'> = E_k <d|\phi_k^+> + E_k \,a_d^{(+)} \;. \tag{10}$$

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 emphsized 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 position to discuss the meaning of the reamining terms of equation (12). The third term of (12) describes impurity induced s-d mixing, which compares formally to the second term just by replacing the mixing potential Δ by the "reduced" impurity potential $U(1-\Sigma_\alpha|\alpha><\alpha|)$. Finally the last term describes pure d-d-sacttering, which is the responsible for pilling-up d-states at the top of the band or for the existence of a d-bound states outside the d-band. To solve equation (12) for the coefficents $\{a_d^{(+)}\}$ is then equivalent to solve the pure d-d impurity problem defined by matrix elements $<d|U|d'>$. At this point we introduce for simplicity the approximation of localized impurity potentials for which $<d|U|d'> \cong \tilde{U}$, where $\tilde{U}$ is independent of d, d'. Within this approximation it is possible to obtain a quite simple expression for the $a_d^{(+)}$ coefficients without disturbing significantly the physics of the problem. It follows then form (12) that:

$$\Sigma_{d'} \; a_{d'}^{(+)} = -\Sigma_{d'}<d'|\phi_k^+> + \Sigma_{d'} \frac{<d'|\Delta|\phi_k^+>}{E_{d'}- E_k} + \sum_{d'} \frac{<d'|U(1-\Sigma_\alpha|\alpha><\alpha|)|\phi_k^+>}{E_k - E_{d'}} +$$

$$+ \tilde{U} \; \Sigma_d \frac{1}{E_k- E_d} \Sigma_{d'} \; a_{d'}^{(+)} . \tag{15}$$

Introducing the function F(E) defined by: $F(E) = \Sigma_d 1/E-Ed$ it follows from (15) that

$$\Sigma_{d'} \; a_{d'}^{(+)} = \frac{1}{1-\tilde{U}F(E_k)} \left\{ -\Sigma_{d'}<d'|\phi_k^+> + \Sigma_{d'} \frac{<d'|\Delta|\phi_k^+>}{E_{d'}-E_k} + \Sigma_{d'} \frac{<d'|U(1-\Sigma_\alpha|\alpha><\alpha|)|\phi_k^+>}{E_k- E_{d'}} \right\}$$
$$\tag{16}$$

$$\{T+V+\Sigma_\alpha(E_k-E_\alpha)|\alpha><\alpha|\}|\phi_k^+> +\Sigma_d \, a_d^{(+)} \, (E_d-\Delta)|d> - \Sigma_d \, E_k \, a_d^{(+)} \, d>$$

$$+ U(1-\Sigma_\alpha|\alpha><\alpha|)|\phi_k^+> + \Sigma_d \, a_d^{(+)} \, U|d> = E_k|\phi_k^+> \qquad (19)$$

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

$$\Sigma_d \, a_d^{(+)} \, (E_d-\Delta)|d> = \left\{-\Sigma_d(E_d-\Delta)|d><d| + \Sigma_d \frac{(E_d-\Delta)|d><d|\Delta}{E_d-E_k}\right\}|\phi_k^+> +\Sigma_d \, a_d^{(+)} \, (U)(E_d-\Delta)|d>$$

$$(20a)$$

$$\Sigma_d \, E_k \, a_d^{(+)} \, |d> = \left\{-\Sigma_d \, E_k|d><d| + \Sigma_d \frac{E_k|d><d|\Delta}{E_d-E_k}\right\}|\phi_k^+> + \Sigma_d \, a_d^{(+)} \, (U) \, E_k|d> \qquad (20b)$$

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

$$\{T+V+ (E_k-E_\alpha)|\alpha><\alpha|\}|\phi_k^+>+ \left\{- \Sigma_d(E_d-\Delta)|d><d|+ \Sigma_d \, E_k|d><d|+ \Sigma_d \frac{(E_d-E_k-\Delta)|d><d|\Delta}{E_d-E_k}\right\}|\phi_k^+>$$

$$+ \Sigma_d \, a_d^{(+)} \, (U)(E_d-\Delta)|d> - \Sigma_d \, a_d^{(+)} \, (U)E_k|d> + U(1-\Sigma_\alpha|\alpha><\alpha|)|\phi_k^+> + \Sigma_d \, a_d^{(+)} \, U|d> = E_k|\phi_k^+>$$

$$(21)$$

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:

$$\left\{T+V+\Sigma_\alpha(E_k-E_\alpha)|\alpha><\alpha|+\Sigma_d(E_k-E_d)|d><d|+\Sigma_d\Delta|d><d|+\Sigma_d|d><d|\Delta \right.$$

$$\left. + \Sigma_d \frac{\Delta|d><d|\Delta}{E_k-E_d}\right\}|\phi_k^+> = \mathcal{H}_{nob}^P|\phi_k^+> \qquad (22)$$

$$U^P = U(1-\Sigma_\alpha|\alpha><\alpha|-\Sigma_d|d><d|)+\Sigma_d \frac{U|d><d|\Delta}{E_d-E_k} + \Sigma_d \frac{(E_d-E_k-\Delta+U)|d><d|U(1-\Sigma_\alpha|\alpha><\alpha|)}{E_k-E_d}$$

$$+\Sigma_d \frac{(E_k-E_d-\Delta+U)|d><d|U}{(E_d-E_k)(1-\tilde{U} F(E_k))}\left[-\Sigma_{d'}|d'><d'| + \Sigma_{d'}\frac{|d'><d'|\Delta}{E_{d'}-E_k} + \Sigma_{d'}\frac{|d'><d'|U(1-\Sigma_\alpha|\alpha><\alpha|)}{E_k-E_{d'}} \right] \quad (27)$$

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

$$(E_k-\mathcal{H}^P_{nob})|\phi^+_k> = U^P|\phi^+_k> \quad (28)$$

or incorporating the out-going behaviour and the condition $\lim_{V\to 0} \phi^+_k >= |\phi_k>$ one obtains the equivalent Lippman-Schwinger equation:

$$|\phi^+_k> = |\phi_k> + \frac{1}{E_k-\mathcal{H}^P_{nob}+i\epsilon} U^P|\phi^+_k> \quad (29)$$

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

INTERPRETATION OF THE EFFECTIVE POTENTIAL

The equivalent problem defined by equations (29) and (27) provides a clear picture of the scattering mechanism 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. From equation (27) one sees that the matrix elements of U^P between plane waves, $<k'|U^P|k>$ involve several contributions (cf. Appendix 1).

To put in pictorial terms let's introduce the following elementary scattering processes:

a) The direct scattering from k to k', in presence of a reduction factor $(1-\Sigma_\alpha|\alpha><\alpha|-\Sigma_d|d><d|)$ as in the case of normal metals without node effects

where $\odot$ $\equiv$ $\bullet$ times $\dfrac{1}{1-\tilde{U}\ F(E_k)}$ and the occurrence of the factor $(1-\tilde{U}\ F(E_k))$ characterizes the usual d-d scattering problem. From this factor one knows if there exists impurity extracted d-bound states which appear in Anderson's model [4] of impurity problems.

Using this notation the effective potential matrix elements can be analyzed in the following processes
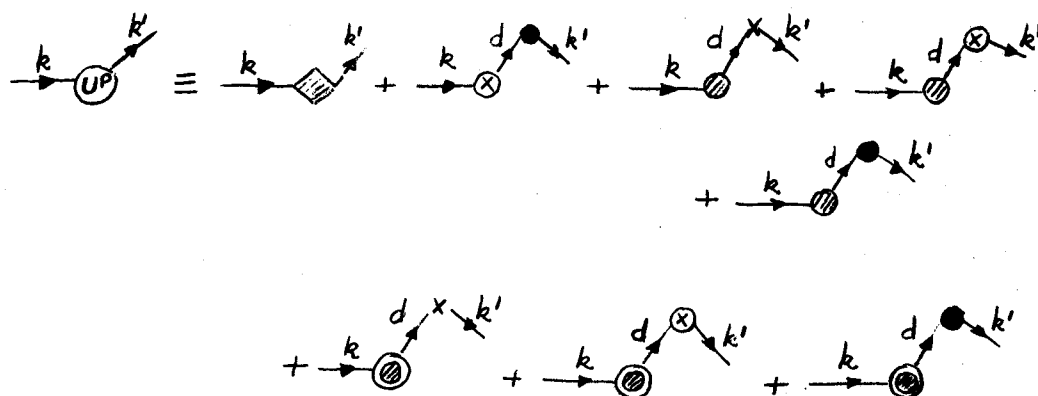
FORMULATION OF THE IMPURITY PROBLEM FOR THE TRANSITION METAL CASE

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, the "true" wave function for energies in the d-like region read:

$$|\psi d\rangle = |d\rangle + (1-\Sigma_\alpha|\alpha\rangle\langle\alpha|)|\phi\rangle \tag{30}$$

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

$$|\phi\rangle = \Sigma_k a_k|k\rangle \tag{31}$$

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

$$(T+V)|\phi\rangle + \Sigma_\alpha(E-E_\alpha)|\alpha\rangle\langle\alpha|\phi\rangle + (E_d-E-\Delta)|d\rangle = E|\phi\rangle \tag{32}$$

$$|\psi_d^+> = \Sigma_{d'} \; a_{d'}^{(+)} |d'> + (1-\Sigma_\alpha|\alpha><\alpha|)|\phi^+> \qquad (34)$$

In equation (34) the coefficients $a_{d'}^{(+)}$ are the solution of the pure tight

binding scattering problem [3] (cf. below), and the scattering conditions read:

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

where $\delta a_{d'}^{(+)}$ describes scattering and reduces to zero in the limit of zero per-

turbation. Quite similarly the scattered pseudo wave function is defined as:

$$|\phi^+> = \Sigma_{k'} \; a_{k'}^{(+)} |k'> \qquad (36)$$

the coefficients $a_{k'}^{(+)}$ being defined as

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

the $a_{k'}$ being the solutions of (30) and (33), and correspond to the pure metal

limit. In these conditions equation (34) can be written as:

$$|\psi_d^{(+)}> = \{|d> +(1-\Sigma_\alpha|\alpha><\alpha|)|\phi>\} + \underset{d'}{\Sigma} \delta a_{d'}^{(+)}|d'> + \{(1-\Sigma_\alpha|\alpha><\alpha|)\underset{k'}{\Sigma} \delta a_{k'}^{(+)}|k'>\} \; . \quad (38)$$

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

$\mathcal{H}^{TB} = T + V_a$, V_a being an atomic like potential, from which the tight binding

of states is derived. Now we introduce the self-consistent impurity potential

$$(T+V+\Sigma_\alpha(E-E_\alpha)|\alpha><\alpha|)|\phi^+> + (E_d-E-\Delta)|d> - E|\phi^+> + U(1-\Sigma_\alpha|\alpha><\alpha|)|\phi^+>$$

$$+ \Sigma_{d'} \delta a_{d'}^{(+)}(U)(E_{d'}-E-\Delta)|d'> + \Sigma_{d'} a_{d'}^{(+)} U|d'> = 0 \qquad (44)$$

The first three terms of equation (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 $U(1-\Sigma_\alpha|\alpha><\alpha|)$. 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 the Scattering Equation by a Perturbation Approach

We firstly substitute equation (36) into equation (44), define $W_0 = = V + \Sigma_\alpha(E-E_\alpha)|\alpha><\alpha|$, to get:

$$\Sigma_{k'} a_{k'}^{(+)}(T+W_0-E_k)|k'> + (E_d-E_k-\Delta)|d> + \Sigma_{k'} a_{k'}^{(+)} U(1-\Sigma_\alpha|\alpha><\alpha|)|k'>$$

$$+ \Sigma_{d'} \delta a_{d'}^{(+)}(U)(E_{d'}-E_k-\Delta)|d'> + U|d> + \Sigma_{d'} \delta a_{d'}^{(+)}(U)U|d'> = 0 \qquad (45)$$

where we which 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 $a_{k'}$ of equation (37), we find from (45):

$$\Sigma_{k'} a_{k'}(T+W_0-E_k)|k'> + (E_d-E_k-\Delta)|d> = 0 \qquad (46)$$

the solution being given by Harrison (first order solution is exemplified in (34). Now it remains to determine the $\delta a_k^{(+)}$ 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 remaing terms. Once one recognizes this, the frist two terms may be replaced by:

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 tight binding scattering terms. The third term describes how already admixed s-like states (through the coefficients $a_{k''}$) are scattered by the "reduced" impurity potential to other s-like states labelled by k'. Hence third terms is typically a s-s scattering term. The fourth term describes how host metal s-d mixing couples scattered d-states to s-like 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.

DISCUSSION

In both cases (transition and noble), the essential features of the approach are the tight binding sums, plane wave expansions and the orthogonality requirements. The host metal s-d mixing effects areise from the self-consistency calculation in order to obtain the actual pure crystal potential V, and this will be supposed to be done in a previous calculation. A very important consequence of the orthogonality requirements in the impurity problem is connected to the fact that plane waves are not orthogonal to core states and the orthogonalization procedure introduce a "reduction factor" in the "bare" impurity potential U, in the form $U(1-\Sigma_\alpha |\alpha><\alpha|)$. 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 as acting in these processes also because:

$$<d|U(1-\Sigma_\alpha |\alpha><\alpha|)|d'> \ = \ <d|U|d'> \ - \ \Sigma_\alpha <d|U|\alpha><\alpha|d'> \ \equiv \ <d|U|d'>$$

$$<k|U(1-\Sigma_\alpha |\alpha><\alpha|)|d \ > \ = \ <k|U|d \ > \ - \ \Sigma_\alpha <k|U|\alpha><\alpha|d \ > \ \equiv \ <k|U|d \ >$$

this should be compared to

waves $\Sigma_t |t><t| = 1$, in equation (29) in order to obtain a tractable equation for the scattering T matrix as discussed in detail in $|I|$.

* * *

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INTRODUCTION

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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 neighbourhood of the Fermi level (cf. fig. 2 and 3).

These d-states introduce further difficulties in the discussion of the alloy electronic structure even in the absence of node effects, so in this work we restrict ourselves to the simplest case of dominant charge effect. The pseudo-potential 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 constructed from atomic d-states are not exact solutions of the complete crystal problem. From Harrison's devellopments 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 shift. It is then 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 well separate the approaches to describe noble and transition metals. In fact, in noble metal cases one has for the states in the neighbourhood 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 contrary, for the transition metal case, the dominant contribution comes from d-like states obtained from tight binding sums as far 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 non-local 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 paralelism between this case and Harrison's transition host problem.

To summarize: for noble alloys again one starts defining the "true" scattering problem, the corresponding pseudo-wave function and the effective impurity potential. The main difference respect to 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 [2]. In this way in the limit of zero impurity perturbation one recovers Harrison's pseudo potential description of the transition host metal.

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We start defining the alloy wave function, assuming from the begining that node effects may be disregarded. The case of impurity and host belonging to different lines of the periodic table may be handled in similar lines to those developped previously (I); the only difference respect to normal metals is that d-states must be included in considering the node effects. We start defining the "true" scattered wave function $|\psi_k^+>$, solution of

$$(T+V+U)|\psi_k^+> = E_k | \psi_k^+ > \tag{1}$$

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)

$$<\alpha|\psi_k^+> = 0 \text{ for all states } |\alpha> \tag{2}$$

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

$$\lim_{U \to 0} |\psi_k^+> = |\psi_k> \tag{3}$$

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

A very convenient way of writting $|\psi_k^+ >$ is provided [2] by an expansion in terms of an overcomplete set of plane waves and tight-binding d-states. In doing so, one automatically fulfills condition (i) since for

$$|\psi> = (1 - \Sigma_\alpha |\alpha><\alpha|)|\phi_k^+> + \Sigma_{d'} a_{d'}^{(+)} |d'> \tag{4}$$

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

$$\Delta |d> = \delta V |d> - <d|\delta V|d>|d> \tag{5}$$

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 a repulsive potential for instance; when acting on d-states this potential, depending on its strength pile up states at the top of the d-band or extracts a d-bound state above it. In both cases, due to s-d mixing (impurity indiced or through the Δ 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:

$$(T+V)|\phi_k^+> - \Sigma_\alpha E_\alpha |\alpha><\alpha|\phi_k^+> + \Sigma_{d'} a_{d'}^{(+)}(T+V)|d'> + U(1-\Sigma_\alpha|\alpha><\alpha|)|\phi_k^+> +$$

$$+ \Sigma_{d'} a_{d'}^{(+)} U|d'> = E_k|\phi_k^+> - \Sigma_\alpha E_k|\alpha><\alpha|\phi_k^+> + \Sigma_{d'} E_k a_{d'}^{(+)}|d'> \tag{6}$$

where in the absence of node effects we used:

$$(T+V)|\alpha > = E_\alpha |\alpha > \qquad (7)$$

Now equation (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 [1]:

$$<d|T+V|\phi_k^+ > = E_d <d|\phi_k^+ > - <d|\Delta|\phi_k^+ > \qquad (8\text{-}a)$$

which follows from:

$$(T+V)|d > = E_d|d > - \Delta|d > \qquad (8\text{-}b)$$

where

$$E_d = <d|T+V|d > \qquad (8\text{-}c)$$

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

$$<d|T+V|d' > = E_d \, \delta_{dd'} - <d|\Delta|d' > \qquad (8\text{-}d)$$

and

$$\Sigma_{d'} \, \alpha_{d'} < d|\Delta|d' > = 0 \qquad (8\text{-}e)$$

for any c-numbers $\{\alpha_{d'}\}$, using the tight-binding approximations.

Performing the calculation through these steps one gets:

$$<d|T+V|\phi_k^+ > + \Sigma_{d'} \, a_{d'}^{(+)} < d|T+V|d'> + <d|U(1-\Sigma_\alpha|\alpha><\alpha|)|\phi_k^+ >$$

$$+ \Sigma_{d'} \, a_{d'}^{(+)} < d|U|d'> = E_k < d|\phi_k^+ > + E_k \, a_d^{(+)} \qquad (9)$$

where use was made of $<\alpha|d > = 0$ for any $|\alpha>$ and $|d>$. Using equations (8-a), (8-d) and (8-e) one rewrites (9) as:

$$E_d <d|\phi_k^+ > - <d|\Delta|\phi_k^+ > + E_d \, a_d^{(+)} + < d|U(1-\Sigma_\alpha|\alpha><\alpha|\phi_k^+ >$$

$$+ \Sigma_{d'} \, a_{d'}^{(+)} <d|U|d'> = E_k <d|\phi_k^+ > + E_k \, a_d^{(+)} \,. \qquad (10)$$

Rearranging terms one gets:

$$(E_k - E_d) a_d^{(+)} = (E_d - E_k)<d|\phi_k^+> - <d|\Delta|\phi_k^+> + <d|U(1-\Sigma_\alpha|\alpha><\alpha|)|\phi_k^+> + \Sigma_{d'} a_{d'}^{(+)}<d|U|d'>$$
(11)

or finally:

$$a_d^{(+)} = -<d|\phi_k^+> + \frac{<d|\Delta|\phi_k^+>}{E_d - E_k} + \frac{<d|U(1-\Sigma_\alpha|\alpha><\alpha|)|\phi_k^+>}{E_k - E_d} + \frac{1}{E_k - E_d}\Sigma_{d'} a_{d'}^{(+)}<d|U|d'>$$
(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 $|\phi_k^+>$, which substituted in (6) provide an effective equation for the scattered pseudo wave function. This means that equation (12) incorporates the solution of the pure d impurity problem and how d-states mix with condution states. In order to get a better feeling of things involved in equation (12) it is interesting to recover the pure metal limit derived by Harrison just taking $U = 0$ in the equation defining the $a_d^{(+)}$'s. If one calls $|\phi_k>$ the pure metal ($U = 0$) limit of the scattered pseudo wave functions and the corresponding coefficients $\{a_d\}$, one gets from (12)

$$a_d = -<d|\phi_k> + \frac{<d|\Delta|\phi_k>}{E_d - E_k}.$$
(13)

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

$$|\psi_k> = (1-\Sigma_\alpha|\alpha><\alpha|)|\phi_k> - \Sigma_{d'}|d'><d'|\phi_k> + \Sigma_{d'} \frac{|d'><d'|\Delta|\phi_k>}{E_{d'} - E_k}$$

$$= (1-\Sigma_\alpha|\alpha><\alpha| - \Sigma_{d'}|d'><d'|)|\phi_k> + \Sigma_{d'} \frac{|d'><d'|\Delta|\phi_k>}{E_{d'} - E_k}.$$
(14)

This expression provides a very simple interpretation of the first two terms of (12). The first term $-<d|\phi_k>$ 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 emphsized 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 position to discuss the meaning of the reamining terms of equation (12). The third term of (12) describes impurity induced s-d mixing, which compares formally to the second term just by replacing the mixing potential Δ by the "reduced" impurity potential $U(1-\Sigma_\alpha |\alpha><\alpha|)$. Finally the last term describes pure d-d-sacttering, which is the responsible for pilling-up d-states at the top of the band or for the existence of a d-bound states outside the d-band. To solve equation (12) for the coeffients $\{a_d^{(+)}\}$ is then equivalent to solve the pure d-d impurity problem defined by matrix elements $<d|U|d'>$. At this point we introduce for simplicity the approximation of localized impurity potentials for which $<d|U|d'> \cong \tilde{U}$, where $\tilde{U}$ is independent of d, d'. Within this approximation it is possible to obtain a quite simple expression for the $a_d^{(+)}$ coefficients without disturbing significantly the physics of the problem. It follows then form (12) that:

$$\Sigma_{d'} \, a_{d'}^{(+)} = -\Sigma_{d'} <d'|\phi_k^+> + \Sigma_{d'} \frac{<d'|\Delta|\phi_k^+>}{E_{d'} - E_k} + \sum_{d'} \frac{<d'|U(1-\Sigma_\alpha|\alpha><\alpha|)|\phi_k^+>}{E_k - E_{d'}} +$$

$$+ \tilde{U} \Sigma_d \frac{1}{E_k - E_d} \Sigma_{d'} \, a_{d'}^{(+)} . \tag{15}$$

Introducing the function F(E) defined by: $F(E) = \Sigma_d 1/E-Ed$ it follows from (15) that

$$\Sigma_{d'} \, a_{d'}^{(+)} = \frac{1}{1-\tilde{U}F(E_k)} \left\{ -\Sigma_{d'} <d'|\phi_k^+> + \Sigma_{d'} \frac{<d'|\Delta|\phi_k^+>}{E_{d'} - E_k} + \Sigma_{d'} \frac{<d'|U(1-\Sigma_\alpha|\alpha><\alpha|)|\phi_k^+>}{E_k - E_{d'}} \right\}$$

$$\tag{16}$$

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

$$a_d^{(+)} = -\langle d|\phi_k^+\rangle + \frac{\langle d|\Delta|\phi_k^+\rangle}{E_d - E_k} + \frac{\langle d|\tilde{U}(1-\Sigma_\alpha|\alpha\rangle\langle\alpha|)|\phi_k^+\rangle}{E_k - E_d}$$

$$+ \frac{\tilde{U}}{(E_k-E_d)(1-\tilde{U}\,F(E_k))}\left\{ -\Sigma_{d'}\langle d'|\phi\rangle + \Sigma_{d'}\frac{\langle d'|\Delta|\phi_k^+\rangle}{E_{d'} - E_k} + \Sigma_{d'}\frac{\langle d'|U(1-\Sigma_\alpha|\alpha\rangle\langle\alpha|)|\phi_k^+\rangle}{E_k - E_{d'}} \right\}$$

(17)

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

$$\Sigma_d \, a_d^{(+)}|d\rangle = \left\{ -\Sigma_d|d\rangle\langle d| + \Sigma_d\frac{|d\rangle\langle d|\Delta}{E_d - E_k} + \Sigma_d\frac{|d\rangle\langle d|U(1-\Sigma_\alpha|\alpha\rangle\langle\alpha|)}{E_k - E_d} \right\}|\phi_k^+\rangle$$

$$+ \Sigma_d\frac{|d\rangle\langle d|U}{(E_k-E_d)(1-\tilde{U}\,F(E_k))}\left\{ -\Sigma_{d'}|d'\rangle\langle d'| + \Sigma_{d'}\frac{|d'\rangle\langle d'|\Delta}{E_{d'} - E_k} + \Sigma_{d'}\frac{|d'\rangle\langle d'|U(1-\Sigma_\alpha|\alpha\rangle\langle\alpha|)}{E_k - E_{d'}} \right\}|\phi_k^+\rangle$$

(18)

The advantage of expression (18) is that it shows clearly that whence $|\phi_k^+\rangle$, is obtained from a scattering type of calculation, by operating with **known operators** one obtains directly the d-like part of the wave function. Equation (18) is also the central step for obtaining the equivalent scattering equation for $|\phi_k^+\rangle$ because of its special form:

$$\Sigma_d \, a_d^{(+)}|d\rangle = \text{Operator } |\phi_K^+\rangle$$

Now, next step is to obtain the equivalent equation for the scattered pseudo wave function $|\phi_k^+\rangle$. To do that we return to equation (6) which is now rewritten as:

$$\{T+V+\Sigma_\alpha(E_k-E_\alpha)|\alpha><\alpha|\}|\phi_k^+> +\Sigma_d\ a_d^{(+)}\ (E_d-\Delta)|d> - \Sigma_d\ E_k\ a_d^{(+)}\ d>$$

$$+ U(1-\Sigma_\alpha|\alpha><\alpha|)|\phi_k^+> + \Sigma_d\ a_d^{(+)}\ U|d> = E_k|\phi_k^+> \tag{19}$$

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

$$\Sigma_d\ a_d^{(+)}\ (E_d-\Delta)|d> = \left\{-\Sigma_d(E_d-\Delta)|d><d| + \Sigma_d\ \frac{(E_d-\Delta)|d><d|\Delta}{E_d-E_k}\right\}|\phi_k^+> +\Sigma_d\ a_d^{(+)}\ (U)(E_d-\Delta)|d> \tag{20a}$$

$$\Sigma_d\ E_k\ a_d^{(+)}|d> = \left\{-\Sigma_d\ E_k|d><d| + \Sigma_d\ \frac{E_k|d><d|\Delta}{E_d-E_k}\right\}|\phi_k^+> + \Sigma_d\ a_d^{(+)}\ (U)\ E_k|d> \tag{20b}$$

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

$$\{T+V+(E_k-E_\alpha)|\alpha><\alpha|\}|\phi_k^+>+ \left\{-\Sigma_d(E_d-\Delta)|d><d|+ \Sigma_d\ E_k|d><d|+ \Sigma_d\ \frac{(E_d-E_k-\Delta)|d><d|\Delta}{E_d-E_k}\right\}|\phi_k^+>$$

$$+ \Sigma_d\ a_d^{(+)}\ (U)\ (E_d-\Delta)|d> - \Sigma_d\ a_d^{(+)}\ (U)E_k|d> + U(1-\Sigma_\alpha|\alpha><\alpha|)|\phi_k^+> + \Sigma_d\ a_d^{(+)}\ U|d> = E_k|\phi_k^+> \tag{21}$$

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:

$$\left\{T+V+\Sigma_\alpha(E_k-E_\alpha)|\alpha><\alpha|+\Sigma_d(E_k-E_d)|d><d|+\Sigma_d\Delta|d><d|+\Sigma_d|d><d|\Delta\ +\right.$$

$$\left.+ \Sigma_d\ \frac{\Delta|d><d|\Delta}{E_k-E_d}\right\}|\phi_k^+> =\mathcal{H}_{nob}^P|\phi_k^+> \tag{22}$$

Using this result, equation (21) can be rewritten as:

$$(E_k - \mathcal{H}^P_{nob}) |\phi^+_k> = U(1 - \Sigma_\alpha |\alpha><\alpha|) |\phi^+_k> \; \Sigma_d \; a^{(+)}_d \; (U) (E_d - E_k - \Delta) |d> + \Sigma_d \; a^{(+)}_d \; U|d> \qquad (23)$$

DETERMINATION OF THE EFFECTIVE IMPURITY POTENTIAL AND THE EQUIVALENT SACTTERING EQUATION

The effective impurity potential is defined in the following way:

$$U^P |\phi^+_k> = \text{right hand side of (23)}$$

More explicitly one gets:

$$U^P |\phi^+_k> = U(1 - \Sigma_\alpha |\alpha><\alpha|) |\phi^+_k> + \Sigma_d \left\{ -U|d><d| + \frac{U|d><d|\Delta}{E_d - E_k} \right\} |\phi^+_k> \; +$$

$$\Sigma_d \; a^{(+)}_d \; (U) (E_d - E_k - \Delta + U) |d> \qquad (24)$$

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:

$$U(1 - \Sigma_\alpha |\alpha><\alpha| \; -\Sigma_d |d><d|) + \Sigma_d \frac{U|d><d|\Delta}{E_d - E_k} . \qquad (25)$$

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

$$\Sigma_d \; a^{(+)}_d \; (U) (E_d - E_k - +U) |d> = \left\{ \Sigma_d \frac{(E_d - E_k - \Delta + U) |d><d| U(1 - \Sigma_\alpha |\alpha><\alpha|)}{E_k - E_d} \right\} |\phi^+_k >$$

$$+\Sigma_d \frac{(E_d - E_k - \Delta + U) |d><d| U}{(E_d - E_k)(1 - \tilde{U} F(E_k))} \left\{ -\Sigma_{d'} |d'><d'| + \Sigma_{d'} \frac{|d'><d'|\Delta}{E_{d'} - E_k} + \Sigma_{d'} \frac{|d'><d'| U(1 - \Sigma_\alpha |\alpha><\alpha|)}{E_k - E_{d'}} \right\} |\phi^+_k>$$

$$(26)$$

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

$$U^P = U(1-\Sigma_\alpha|\alpha><\alpha|-\Sigma_d|d><d|)+\Sigma_d \frac{U|d><d|\Delta}{E_d-E_k} + \Sigma_d \frac{(E_d-E_k-\Delta+U)|d><d|U(1-\Sigma_\alpha|\alpha><\alpha|)}{E_k-E_d}$$

$$+\Sigma_d \frac{(E_k-E_d-\Delta+U)|d><d|U}{(E_d-E_k)(1-\tilde{U} F(E_k))}\left[- \Sigma_{d'} |d'><d'| + \Sigma_{d'} \frac{|d'><d'|\Delta}{E_{d'}-E_k} + \Sigma_{d'} \frac{|d'><d'|U(1-\Sigma_\alpha|\alpha><\alpha|)}{E_k-E_{d'}} \right] (27)$$

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

$$(E_k-\mathcal{H}^P_{nob})|\phi_k^+> = U^P|\phi_k^+> \tag{28}$$

or incorporating the out-going behaviour and the condition $\lim_{V\to 0} \phi_k^+ >= |\phi_k>$ one obtains the equivalent Lippman-Schwinger equation:

$$|\phi_k^+> = |\phi_k> + \frac{1}{E_k-\mathcal{H}^P_{nob}+i\epsilon} U^P|\phi_k^+> \tag{29}$$

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

INTERPRETATION OF THE EFFECTIVE POTENTIAL

The equivalent problem defined by equations (29) and (27) provides a clear picture of the scattering mechanism 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. From equation (27) one sees that the matrix elements of U^P between plane waves, $<k'|U^P|k>$ involve several contributions (cf. Appendix 1).

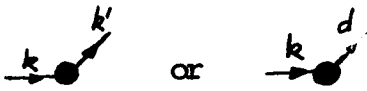To put in pictorial terms let's introduce the following elementary scattering processes:

a) The direct scattering from k to k', in presence of a reduction factor $(1-\Sigma_\alpha|\alpha><\alpha|-\Sigma_d|d><d|)$ as in the case of normal metals without node effects

(as it should be if tight binding states were exact states of the crystal hamil-
tonian) is depicted as:

$$\equiv \langle k'|U(1-\Sigma_\alpha|\alpha\rangle\langle\alpha|-\Sigma_d|d\rangle\langle d|)|k\rangle$$

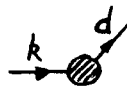b) Bare scattering by the impurity potential U is represented as:

meaning $\langle k'|U|k\rangle$ and $\langle d'|U|k\rangle$ respectively.
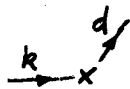
c) Host metal s-d mixing inducing s-d scattering

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

e) The impurity effects reduced by inner shell orthogonalization:

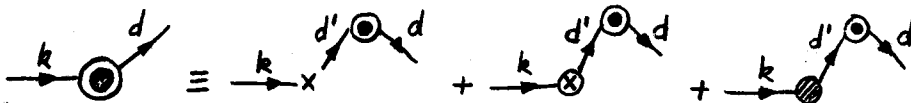$$\equiv \langle d|U(1-\Sigma_\alpha|\alpha\rangle\langle\alpha|)|k\rangle$$

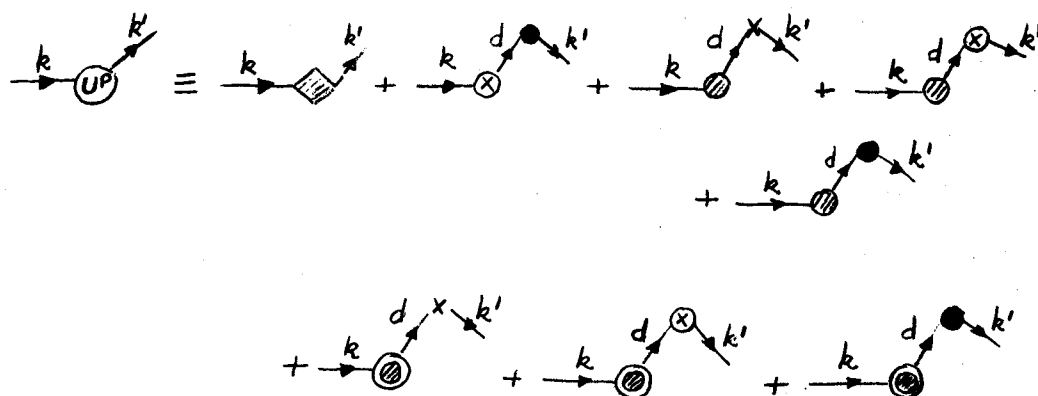f) The matrix elements $\langle k|d\rangle$ are represented by:

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 a s-d mixing involving d-d scattering can be depicted as:

where $\bigodot \equiv \bullet$ times $\dfrac{1}{1-\tilde{U}\,F(E_k)}$ and the occurrence of the factor $(1-\tilde{U}\,F(E_k))$ cha-racterizes the usual d-d scattering problem. From this factor one knows if there exists impurity extracted d-bound states which appear in Anderson's model [4] of impurity problems.

Using this notation the effective potential matrix elements can be analyzed in the following processes

FORMULATION OF THE IMPURITY PROBLEM FOR THE TRANSITION METAL CASE

A) Pure Metal Results

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

$$|\psi d\rangle = |d\rangle + (1-\Sigma_\alpha|\alpha\rangle\langle\alpha|)|\phi\rangle \qquad (30)$$

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

$$|\phi\rangle = \Sigma_k a_k |k\rangle \qquad (31)$$

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

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

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)):

$$\Sigma_{k'} \, a_{k'} \left(\frac{k'^2}{2m} - E \right) |k'> + \Sigma_{k'} \, a_{k'} V |k'> + \sum_{k',\alpha} a_{k'} (E-E_\alpha) |\alpha><\alpha|k'> + (E_d - E - \Delta) |d> = 0$$

(33)

to obtain (for instance to first order in Δ): $a_k \cong - \dfrac{<k|\Delta|d>}{E_d - E_k}$, E_k being defined as $E_k = \dfrac{k^2}{2m} + <k|W|>k$ where W is the noble metal pseudo potential (cf. expression 22). It will turn out in the following that equation (33) plays an essential role in incorporating boundary conditions (zero impurity potential limit) in the scattering problem.

B) Definition of the Impurity Problem

One starts incorporating in the problem three different aspects:

1. 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 (dominant charge effects);

2. Since in the limit of zero s-d mixing, equation (30) for $|\psi_d>$ reduces to the tight binding limit $|d>$, it will be imposed that the scattering solution $|\psi_d^+>$ is 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.

3. The new pseudo wave function $|\phi^+>$ involves also scattering requirements that means out-going behaviour; 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:

$$|\psi_d^+> = \Sigma_{d'} \ a_{d'}^{(+)} |d'> + (1-\Sigma_\alpha |\alpha><\alpha|)|\phi^+> \qquad (34)$$

In equation (34) the coefficients $a_{d'}^{(+)}$ are the solution of the pure tight

binding scattering problem [3] (cf. below), and the scattering conditions read:

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

where $\delta a_{d'}^{(+)}$ describes scattering and reduces to zero in the limit of zero per-

turbation. Quite similarly the scattered pseudo wave function is defined as:

$$|\phi^+> = \Sigma_{k'} \ a_{k'}^{(+)} |k'> \qquad (36)$$

the coefficients $a_{k'}^{(+)}$ being defined as

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

the $a_{k'}$ being the solutions of (30) and (33), and correspond to the pure metal

limit. In these conditions equation (34) can be written as:

$$|\psi_d^{(+)}> = \{|d> +(1-\Sigma_\alpha |\alpha><\alpha|)|\phi>\} + \underset{d'}{\Sigma} \delta a_{d'}^{(+)} |d'> + \{(1-\Sigma_\alpha |\alpha><\alpha|)\underset{k'}{\Sigma} \delta a_{k'}^{(+)} |k'>\} \ . \qquad (38)$$

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

$\mathcal{H}^{TB} = T + V_a$, V_a being an atomic like potential, from which the tight binding

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:

$$|d^+> = |d> + \frac{1}{E-\mathcal{H}^{TB}+i\varepsilon} U|d^+> \tag{39}$$

with

$$|d^+> = \Sigma_{d'} \, a_{d'}^{(+)} |d'> \, , \, a_{d'}^{(+)} = \delta_{dd'} + \delta_{dd'}^{(+)}$$

The general solution of the problem (39) is given in [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 the Scattered Pseudo Wave Function

One starts from the usual equation:

$$(T+V+U)|\psi_d^{(+)}> = E|\psi_d^{(+)}> \tag{40}$$

Substituting (34) in (40) one gets:

$$(T+V)|\phi^+>+U|\phi^+>-\Sigma_\alpha(T+V)|\alpha><\alpha|\phi^+>-U\Sigma_\alpha|\alpha><\alpha|\phi^+> + \Sigma_{d'} \, a_{d'}^{(+)} (T+V)|d'>$$

$$+ \Sigma_{d'} \, a_{d'}^{(+)} U|d'> = \Sigma_{d'} \, a_{d'}^{(+)} E|d'> + E|\phi^+> - \Sigma_\alpha E|\alpha><\alpha|\phi^+> \tag{41}$$

Using equations (7), (8b) one has:

$$\Sigma_\alpha(T+V)|\alpha><\alpha|\phi^+> = \Sigma_\alpha E_\alpha|\alpha><\alpha|\phi^+> \tag{42a}$$

$$\Sigma_{d'} \, a_{d'}^{(+)} (T+V)|d'> = \Sigma_{d'} \, a_{d'}^{(+)} (E_{d'}-\Delta)|d'> \tag{42b}$$

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

$$(T+V+\Sigma_\alpha(E-E_\alpha)|\alpha><\alpha|)|\phi^+>+U(1-\Sigma_\alpha|\alpha><\alpha|)|\phi^+> +\Sigma_{d'} \, a_{d'}^{(+)} (E_{d'}-E-\Delta)|d'>$$

$$+ \Sigma_{d'} \, a_{d'}^+ U|d'> = E|\phi^+> \tag{43}$$

At this point it is very convenient to use (35) in order to separate the impurity dependent terms of $a_{d'}^{(+)}$; equation (43) becomes finally:

$$(T+V+\Sigma_\alpha (E-E_\alpha)|\alpha><\alpha|)|\phi^+> + (E_d-E-\Delta)|d> - E|\phi^+> + U(1-\Sigma_\alpha|\alpha><\alpha|)|\phi^+>$$

$$+ \sum_{d'} \delta a_{d'}^{(+)}(U)(E_{d'}-E-\Delta)|d'> + \sum_{d'} a_{d'}^{(+)} U|d'> = 0 \qquad (44)$$

The first three terms of equation (44), being the limit for zero impurity pertur-bation 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 $U(1-\Sigma_\alpha|\alpha><\alpha|)$. 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 the Scattering Equation by a Perturbation Approach

We firstly substitute equation (36) into equation (44), define $W_o = = V + \Sigma_\alpha (E-E_\alpha)|\alpha><\alpha|$, to get:

$$\Sigma_{k'} a_{k'}^{(+)}(T+W_o-E_k)|k'> + (E_d-E_k-\Delta)|d> + \Sigma_{k'} a_{k'}^{(+)} U(1-\Sigma_\alpha|\alpha><\alpha|)|k'>$$

$$+ \sum_{d'} \delta a_{d'}^{(+)}(U)(E_{d'}-E_k-\Delta)|d'> + U|d> + \sum_{d'} \delta a_{d'}^{(+)}(U)U|d'> = 0 \qquad (45)$$

where we which 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 solu-tion of (45) must correspond to Harrison's determination of the s-d admixing coefficients $a_{k'}$ of equation (37), we find from (45):

$$\Sigma_{k'} a_{k'}(T+W_o-E_k)|k'> + (E_d-E_k-\Delta)|d> = 0 \qquad (46)$$

the solution being given by Harrison (first order solution is exemplified in (34). Now it remains to determine the $\delta a_k^{(+)}$ 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 remaing terms. Once one recognizes this, the frist two terms may be replaced by:

$$\Sigma_{k'} \ \delta a_{k'}^{(+)} (E_{k'} - E_k) | k'> \tag{47}$$

where $E_{k'}$, E_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 n-th order in the perturbation U one gets:

$$\sum_{k''} \delta a_{k''}^{(+)(n)} (E_{k''} - E_k) | k''> + \sum_{k''} \delta a_{k''}^{(+)(n-1)} U(1 - \sum_{\alpha} |\alpha><\alpha|) | k''>$$

$$+ \sum_{d'} \delta a_{d'}^{(+)(n)} (U) (E_{d'} - E_k - \Delta) | d'> + \sum_{d'} a_{d'}^{(+)(n-1)} (U) U | d'> = 0 \tag{48}$$

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 (40), $\delta a_{k''}^{(+)(0)} = a_{k''}$, solution of the pure metal problem as given by Harrison. Multiplying everything by a state $k'>$ one gets:

$$\delta a_{k'}^{(+)(n)} = \sum_{k''} \delta a_{k''}^{(+)(n-1)} \frac{<k'|U(1-\sum_{\alpha}|\alpha><\alpha|)|k''>}{E_k - E_{k'} + i\epsilon} + \sum_{d'} \delta a_{d'}^{(+)(n)} (U) \frac{<k'|E_{d'} - E_k - \Delta|d'>}{E_k - E_{k'} + i\epsilon}$$

$$+ \sum_{d'} a_{d'}^{(+)(n-1)} (U) \frac{<k'|U|d'>}{E_k - E_{k'} + i\epsilon} \tag{49}$$

where the outgoing conditions are incorporated through the $+i\epsilon$ in the denominator insuring that $\sum_{k'} \delta a_{k'}^{(+)(n)} (U) k'>$ has an outgoing behaviour.

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

$$|\psi_d^+> = \{|d> + (1 - \sum_{\alpha} |\alpha><\alpha|) |\phi>\} + \sum_{d'} \delta a_{d'}^{(+)} (U) |d'>$$

$$+ (1 - \sum_{\alpha} |\alpha><\alpha|) \sum_{k'',k'} a_{k''} \frac{<k'|U(1-\sum_{\alpha}|\alpha><\alpha|) k''>}{E_k - E_{k'} + i\epsilon} |k'> + (1 - \sum_{\alpha} |\alpha><\alpha|) \times$$

$$\times \sum_{k',d'} \delta a_{d'}^{(1)} (U) \frac{<k'|E_{d'} - E_k - \Delta|d'>}{E_k - E_{k'} + i\epsilon} |k'> + (1 - \sum_{\alpha} |\alpha><\alpha|) \sum_{k'} \frac{<k'|U|d>}{E_k - E_{k'} + i\epsilon} |k'> \tag{50}$$

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 tight binding scattering terms. The third term describes how already admixed s-like states (through the coefficients $a_{k''}$) are scattered by the "reduced" impurity potential to other s-like states labelled by k'. Hence third terms is typically a s-s scattering term. The fourth term describes how host metal s-d mixing couples scattered d-states to s-like 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.

DISCUSSION

In both cases (transition and noble), the essential features of the approach are the tight binding sums, plane wave expansions and the orthogonality requirements. The host metal s-d mixing effects areise from the self-consistency calculation in order to obtain the actual pure crystal potential V, and this will be supposed to be done in a previous calculation. A very important consequence of the orthogonality requirements in the impurity problem is connected to the fact that plane waves are not orthogonal to core states and the orthogonaliza-tion procedure introduce a "reduction factor" in the "bare" impurity potential U, in the form $U(1-\Sigma_\alpha|\alpha><\alpha|)$. 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 as acting in these processes also because:

$$<d|U(1-\Sigma_\alpha|\alpha><\alpha|)|d'> = <d|U|d'> - \Sigma_\alpha <d|U|\alpha><\alpha|d'> \equiv <d|U|d'>$$

$$<k|U(1-\Sigma_\alpha|\alpha><\alpha|)|d > = <k|U|d > - \Sigma_\alpha <k|U|\alpha><\alpha|d > \equiv <k|U|d >$$

this should be compared to

$$<k|U(1-\Sigma_\alpha|\alpha><\alpha|)|k'> = <k|U|k'> - \Sigma_\alpha<k|U|\alpha><\alpha|k'> \neq <k|U|k'>$$

reflecting then non-orthogonality effects.

* * *

APPENDIX 1

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 equation (27)

$$<k'|U^P|k> = <k'|U(1-\Sigma_\alpha|\alpha><\alpha| -\Sigma_d|d><d|)|k> + \Sigma_d \frac{<k'|U|d><d|\Delta|k>}{E_d - E_k} -$$

$$-\Sigma_d<k'|d><d|U(1-\Sigma_\alpha|\alpha><\alpha|)|k> - \Sigma_d \frac{<k'|\Delta|d><d|U(1-\Sigma_\alpha|\alpha><\alpha|)|k>}{E_k - E_d} +$$

$$+ \Sigma_d \frac{<k'|U|d><d|U(1-\Sigma_\alpha|\alpha><\alpha|)|k>}{E_k - E_d}$$

$$- \Sigma_d <k'|d> \frac{<d|U}{1-\tilde{U} F(E_k)} \left\{ \Sigma_{d'} |d'><d'|k> + \Sigma_{d'} \frac{|d'><d'|\Delta|k>}{E_{d'} - E_k} + \Sigma_{d'} \frac{|d'><d'|U(1-\Sigma_\alpha|\alpha><\alpha|)|k>}{E_k - E_{d'}} \right\}$$

$$- \Sigma_d \frac{<k'|\Delta|d>}{E_d - E_k} \frac{<d|U}{1-\tilde{U} F(E_k)} \left\{ \Sigma_{d'}|d'><d'|k> + \Sigma_{d'} \frac{|d'><d'|\Delta|k>}{E_{d'} - E_k} + \Sigma_{d'} \frac{|d'><d'|U(1-\Sigma_\alpha|\alpha><\alpha|)|k>}{E_k - E_{d'}} \right\}$$

$$+ \Sigma_d \frac{<k'|U|d>}{E_d - E_k} \frac{<d|U}{1-\tilde{U} F(E_k)} \left\{ \Sigma_{d'} |d'><d'|k> + \Sigma_{d'} \frac{|d'><d'|\Delta|k>}{E_{d'} - E_k} + \Sigma_{d'} \frac{|d'><d'|U(1-\Sigma_\alpha|\alpha><\alpha|)k>}{E_k - E_{d'}} \right\}$$
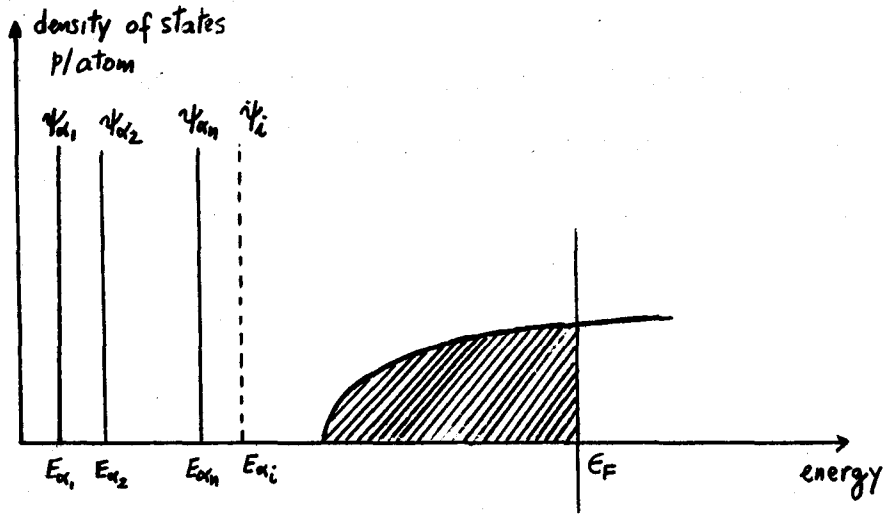
These matrix elements are important since one introduces the complete set of planes

waves $\Sigma_t |t><t| = 1$, in equation (29) in order to obtain a tractable equation for the scattering T matrix as discussed in detail in $|I|$.
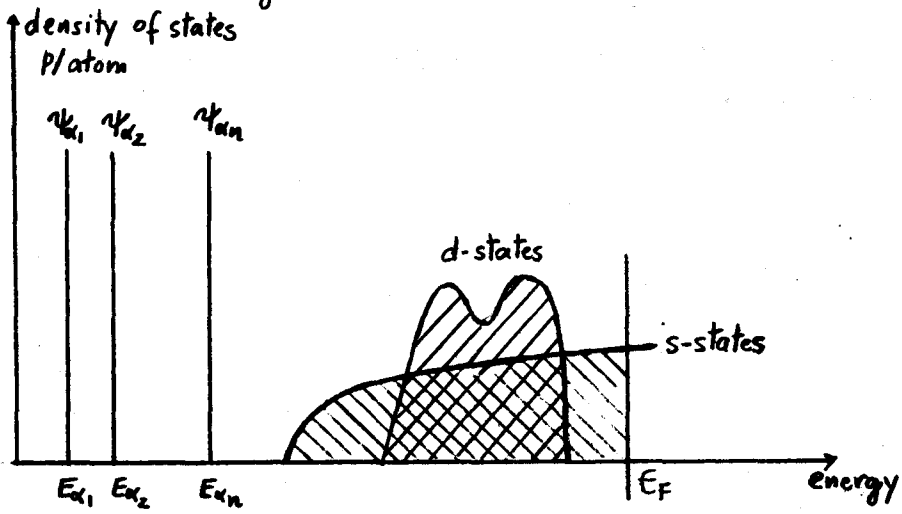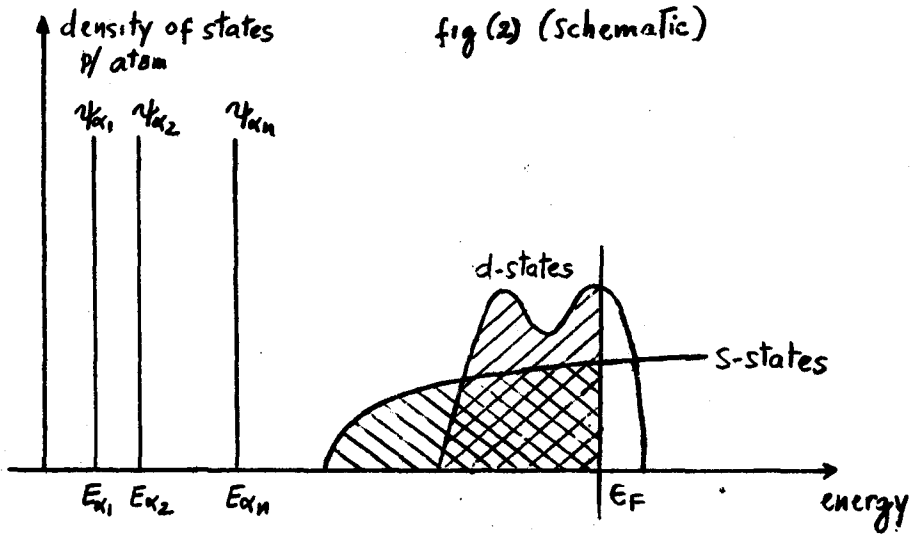
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density of states p/atom

E_{α_1} E_{α_2} E_{α_n} E_{α_i} ϵ_F energy

fig(1) (schematic)

density of states p/atom

d-states
s-states

E_{α_1} E_{α_2} E_{α_n} ϵ_F energy

fig (2) (schematic)

density of states p/atom

d-states
s-states

E_{α_1} E_{α_2} E_{α_n} ϵ_F energy

(fig 3) (Schematic)