PSEUDO-POTENTIAL APPROACH OF NORMAL METAL BASED ALLOYS

by

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INTRODUCTION

The impurity problem in metals involves, as it is well known, two different aspects. Firstly one needs a precise description of the electronic structure of the host, through a theoretical band calculation. Secondly, the self-consistent solution of the scattering problem defined by the host metal hamiltonian and the impurity potential, msut 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 line of the periodic table to which the impurity atoms belong. The later manifest itself through the supplementary 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 difficult 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 litterature [1]; 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 (as the square well) show considerable success in describing situations where the important parameter associated to the impurities is the charge difference [2]. On the contrary, when impurity and host belong to the same column of the periodic table, this picture gives quite inaccurate results [2]; 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 [3] within the tight-binding approximation, using a phenomenological impurity potential, which is determined self-consistently, but again only the cases where the charge differen ce effects are assumed to play the dominant role are considered in detail.

However, several experimental results (in particular Isomer shift data [4], suggest that a quite systematic behaviour can be observed, considering 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 pseudo-atom approach of Ziman [5] is the simplest one which takes into account the details of the host and impurity atoms. However, the pseudo-atom approach for alloys ignore to a certain extend the details of the scattering mechanisms, being then not directly applicable to local properties as for instance Isomer Shift calculations.

In last years, pseudo-potential theory has shown to be a very powerful tool to discuss metallic systems, and in particular it has been extended to include noble and transition metals [6]. It is the central point of pseudo-potential approach to include explicitly the inner shell states (through a self-consistent atomic like calculation), the orthogonality require ment between conduction and inner shell states being automatically satisfied. Since the "node effect" involves essentially these closed shell states, it seems natural to start from the pesudo potential 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 pseudo-potential scheme for normal metal hosts, the case of noble and transition metals being discussed in a forthcoming paper. We adopt the following philosophy: firstly 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. Next

step, and this is the essence of the approach, is to obtain an equivalent scaterring equation for a suitably defined pseudo wave function. This equation is obtained 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 non-local 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.

FORMULATION OF THE PROBLEM

a) Pure Metal (Main Results Of The Pseudo-Potential Approach)

In order to precise the notation and the ideas underlying the pseudo-potential method we start summarizing the main results for the pure metal case. The pure metal, self-consistent one electron potential $V(r)$ is assumed to be given; the one electron states (inner and conduction) satisfy respectively:

$$(T+V)|\alpha\rangle = E_{\alpha}|\alpha) \qquad (1-a)$$

$$(T+V)|\psi_{k}\rangle = E_{k}|\psi_{k} \qquad (1-b)$$

the inner shell states $|\alpha\rangle$ being orthogonal to the condution

states $|\psi_k\rangle$. The pseudo wave functions are defined by:

$$|\psi_k\rangle = (1 - \sum_\alpha |\alpha\rangle\langle\alpha|)|\phi_k\rangle \qquad (2)$$

so the orthogonality requirement is automatically satisfied.
Substituting (2) in (1-b) one verifies that the pseudo wave
function $|\phi_k\rangle$ satisfies:

$$\mathcal{H}_o^p|\phi_k\rangle = \left\{ T + V + \sum_\alpha (E_k - E_\alpha)|\alpha\rangle\langle\alpha| \right\} |\phi_k\rangle = E_k|\phi_k\rangle . \qquad (3)$$

Once the solutions of (3) are obtained, substituting on (2) one
gets the conduction states $|\psi_k\rangle$ to the desired degree of ac-
curacy. One should note that equations (1-a) and (3) involve a
self-consistency problem in the sense that the energies E_α and
the wave functions $|\alpha\rangle$ are not "a priori" known. Usually one
starts from free ion results for $|\alpha\rangle$ and introduces corrections
until self-consistency is achieved.

b) <u>Definition Of The Impurity Problem</u>

An impurity entering substitutionally in a otherwise perfect
normal metal, introduces in the above formulation two essential
modifications:

i)   It appears in equation (1-b) a self-consistent impurity
one electron potential $U(r)$, 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 start discuss-

ing them in a certain detail. We begin precising the nature of
the alloy core states, introducing the following natation for
them:

$$|\bar{\alpha}\rangle = |\vec{R}_\lambda, \ell, m, m\rangle \qquad (4)$$

In expression (4), $\vec{R}_\lambda$ is the position vector of the λ atom, the
set $\{1,m,n\}$ being the usual quantum numbers specifying atomic
like functions. If the impurity is introduced at the origin
$(\vec{R}_\lambda = 0)$ we separate the alloy core states into two groups:

i11) At the impurity site, one may have in the involved $|\bar{\alpha}\rangle$
quantum numbers $\{1,m,n\}$ that do not appear in the pure metal.
This is the case when the impurity and host belong to different
lines of the periodic table, since the potential is then enough
attractive (or repulsive) to introduce (or remove) some new
closed shell states. However, if impurity and host belong to
the same line, one has at $\vec{R}_\lambda = 0$ the same angular quantum num-
bers, but probably different radial parts.

i12) 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 too much
affected 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. The one-electron ha-
miltonian for the alloy being given by:

$$\mathcal{H} = T + V + U \qquad (5-a)$$

we define the scattering states $|\psi_k^+\rangle$ as the out-going solutions

of the Schrödinger equation:

$$(T + V + U)|\psi_k^+ = E_k|\psi_k^+\rangle \qquad (5\text{-}b)$$

Besides the out-going requirement, the states $|\psi_k^+\rangle$ must also satisfy:

$$\langle\bar{\alpha}|\psi_k^+\rangle = 0 \quad \text{for all states } |\bar{\alpha}\rangle. \qquad (5\text{-}c)$$

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

$$\Delta\rho(\vec{r}) = \sum_{k_{occ}} \left\{|\langle r|\psi_k^+\rangle|^2 - |\langle r|\psi_k\rangle|^2\right\} \qquad (6)$$

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

$$q^2 U(q) = 4\pi(Z + \Delta\rho(q)) \qquad (7)$$

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

c) **Definition Of The Mixing Potential**

The above formulation of the scattering states involve the inner shell states $|\bar{\alpha}\rangle$ through the orthogonality condition (5c), so one needs the alloy counterpart of equation (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 defining the states $|\bar{\alpha}\rangle$ as the solutions of an "atomic like" Schröedinger equation:

$$(T + \bar{V})|\bar{\alpha}\rangle = \bar{E}_{\bar{\alpha}} |\bar{\alpha}\rangle \qquad (8\text{-}a)$$

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

$$\bar{V}(\lambda) = V + \delta V(\lambda) \qquad (8\text{-}b)$$

The λ-dependence (position of the atom in the lattice) indicates that different solutions are expected at the impurity and next neighbours. Now we proceed defining $\delta V(\lambda)$, considering firstly the impurity site. Let V_i^{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 equations (8a) and (8b) as:

$$\bar{V}(0) = V_i^{ion} + V_r \qquad (8\text{-}c)$$

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

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

Comparing with equation (8-b) one gets for

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

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

$$\delta V(\lambda) = V_{screen} \tag{9-c}$$

In conclusion equations (9-b) and (9-c) together with (8-a) and (8-b) define completely the solutions $|\bar{\alpha}\rangle$, $\overline{E}_{\bar{\alpha}}$ 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_{screen}. Using these formulae it is possible now to calculate $(T+V)|\bar{\alpha}\rangle$ through the following steps:

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

$$E_{\bar{\alpha}} = \langle\bar{\alpha}|T+V|\bar{\alpha}\rangle = \langle\bar{\alpha}|T+\overline{V}|\bar{\alpha}\rangle - \langle\bar{\alpha}|\delta V|\bar{\alpha}\rangle = \overline{E}_{\bar{\alpha}} - \langle\bar{\alpha}|\delta V|\bar{\alpha}\rangle \tag{10-a}$$

2) Define the mixing potential $\Delta(\alpha)$ by:

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

3) Now one calculates:

$$(T+V)|\bar{\alpha}\rangle = (T+\overline{V})|\bar{\alpha}\rangle - \delta V(\lambda)|\bar{\alpha}\rangle = \overline{E}_{\bar{\alpha}}|\bar{\alpha}\rangle - \delta V(\lambda)|\bar{\alpha}\rangle$$

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

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

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 it can be seen from (10-b).

d) <u>Definition Of The Pseudo Wave Functions And Equivalent Equation</u>.

We begin defining the scattering pseudo wave functions by:

$$|\psi_k^+\rangle = (1 - \sum_{\bar{\alpha}} |\bar{\alpha}\rangle\langle\bar{\alpha}|)|\phi_k^+\rangle \qquad (12\text{-}a)$$

$|\psi_k^+\rangle$ being the "true" scattering wave function defined in (5-b). It should be emphasized that the orthogonality condition (5-c) is automatically satisfied in (12-a) since:

$$\langle\bar{\alpha}'|\psi_k^+\rangle = \langle\bar{\alpha}'|\phi_k^+\rangle - \sum_{\bar{\alpha}}\langle\bar{\alpha}|\phi_k^+\rangle\delta_{\bar{\alpha}\bar{\alpha}'} = 0 \qquad (12\text{-}b)$$

Next step is then to obtain the scattering equation for $|\phi_k^+\rangle$; to do that one substitutes (12-a) in (5-b) to get:

$$(T+V)|\phi_k^+\rangle - \sum_{\bar{\alpha}}(T+V)|\bar{\alpha}\rangle\langle\bar{\alpha}|\phi_k^+\rangle + U(1-\sum_{\bar{\alpha}}|\bar{\alpha}\rangle\langle\bar{\alpha}|)|\phi_k^+\rangle =$$
$$= E_k|\phi_k^+\rangle - \sum_{\bar{\alpha}} E_k|\bar{\alpha}\rangle\langle\bar{\alpha}|\phi_k^+\rangle . \qquad (13)$$

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

$$(T+V)|\phi_k^+\rangle - \sum_{\bar{\alpha}} E_{\bar{\alpha}}|\bar{\alpha}\rangle\langle\bar{\alpha}|\phi_k^+\rangle + \sum_{\bar{\alpha}} \Delta(\lambda)|\bar{\alpha}\rangle\langle\bar{\alpha}|\phi_k^+\rangle + U(1-\sum_{\bar{\alpha}}|\bar{\alpha}\rangle\langle\bar{\alpha}|)|\phi_k^+\rangle \qquad (14\text{-}a)$$

By adding and subtracting $\sum_{\alpha} E_\alpha|\alpha\rangle\langle\alpha|\phi_k^+\rangle$, $|\alpha\rangle$ being the pure metal inner shell states one gets:

$$(T+V-\sum_{\alpha} E_\alpha|\alpha\rangle\langle\alpha|)|\phi_k^+\rangle + \left\{\sum_{\alpha} E_\alpha|\alpha\rangle\langle\alpha| - \sum_{\bar{\alpha}} E_{\bar{\alpha}}|\bar{\alpha}\rangle\langle\bar{\alpha}|\right\}|\phi_k^+\rangle$$
$$+ \sum_{\bar{\alpha}} \Delta(\lambda)|\bar{\alpha}\rangle\langle\bar{\alpha}|\phi_k^+\rangle + U(1-\sum_{\bar{\alpha}}|\bar{\alpha}\rangle\langle\bar{\alpha}|)|\phi_k^+\rangle \qquad (14\text{-}b)$$

Quite similarly, the right hand side of (13) can be transformed to give:

$$E_k|\phi_k^+\rangle - \sum_{\alpha} E_k|\alpha\rangle\langle\alpha|\phi_k^+\rangle + \left[E_k\sum_{\alpha}|\alpha\rangle\langle\alpha| - E_k\sum_{\bar{\alpha}}|\bar{\alpha}\rangle\langle\bar{\alpha}|\right]|\phi_k^+\rangle \qquad (14\text{-}c)$$

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

hamiltonian $\mathcal{H}_o^p = T+V+\sum_\alpha (E_k-E_\alpha)|\alpha\rangle\langle\alpha|$ and defining the effective, non local impurity potential U^p by:

$$U^p = U(1-\sum_{\bar\alpha}|\bar\alpha\rangle\langle\bar\alpha|) + \left\{\sum_\alpha E_\alpha|\alpha\rangle\langle\alpha| - \sum_{\bar\alpha}E_{\bar\alpha}|\bar\alpha\rangle\langle\bar\alpha|\right\} - E_k\left\{\sum_\alpha|\alpha\rangle\langle\alpha| - \sum_{\bar\alpha}|\bar\alpha\rangle\langle\bar\alpha|\right\} +$$

$$+ \sum_{\bar\alpha} \Delta(\lambda)|\bar\alpha\rangle\langle\bar\alpha| \qquad (14\text{-}d)$$

one gets:

$$(E_k-\mathcal{H}_o^p)|\bar\Phi_k^+\rangle = U^p|\bar\Phi_k^+\rangle . \qquad (15\text{-}a)$$

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

$$\lim_{\substack{V \to 0 \\ |\bar\alpha\rangle \to |\alpha\rangle}} |\bar\Phi_k^+\rangle = \Phi_k\rangle \qquad (15\text{-}b)$$

where $|\Phi_k\rangle$ is the solution of equation (3), and the out-going behaviour of the scattered wave functions. These two conditions are fullfilled if instead of (15-a) one writes:

$$|\bar\Phi_k^+\rangle = |\Phi_k\rangle + \frac{1}{E_k-\mathcal{H}_o^p+i} V^p|\bar\Phi_k^+\rangle \qquad (16)$$

Equation (16) is the Lippman-Schwinger equation for pseudo wave functions. At this point it is worthwile to rewrite (16) in coordinate space and to introduce the transition amplitudes. Following Harrison |6| it will be assumed that the pure metal inner states $|\alpha\rangle$ are accurate enough to allow the representation of $|\Phi_k\rangle$ by a single plane wave. ·Although not essential, this assumption simplifies the following calculations. Multiply

ing equation (16) by $|r\rangle$ and defining the effective potential in coordinate space as $U^P(r_1 \ r_2) = \langle r_1|U^P|r_2\rangle$ one obtains remembering that plane waves from a complete set: $(\sum_t |t\rangle\langle t| = 1)$

$$\Phi_k^+(\bar{r}) = e^{ik\cdot r} + \iint dr_1 \ dr_2 \int \frac{dt}{(2\pi)^3} \ \frac{e^{it(r_1-r_2)}}{E_k-E_t+i\epsilon} \ U^P(r_1,r_2)\Phi_k^+(r_2)$$

(17)

The transition amplitude is defined as usually:

$$f(k_1'k) = -\frac{1}{4\pi} \iint dr_1 \ dr_2 \ e^{-ik'\cdot r_1} \ U^P(r_1, r_2)$$

(18)

In terms of the transition amplitudes, the scattered pseudo wave functions reads:

$$\Phi_k^+(r) = e^{ik\cdot r} - 4\pi \int \frac{dt}{(2\pi)^3} \ \frac{f(k,t) \ e^{it\cdot r}}{E_k - E_t + i\epsilon}$$

(19)

showing that these transition amplitudes specify completely the scattered function. It remains to obtain the integral equation from which one calculates the amplitudes $f(k', k)$. 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:

$$T|k\rangle = U^P|\Phi_k^+\rangle$$

(20)

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

$$T(k',k) = \langle k'|T|k\rangle = \langle k'|U^P|\Phi_k^+\rangle = \iint dr_1 dr_2 \langle k'|r_1\rangle \ U^P(r_1 r_2).$$

$$\cdot \ \Phi_k^+(r_2) = -4\pi f(k',k)$$

(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:

$$\langle k' | U^p | \phi_k^+ \rangle = \langle k' | U^p | k \rangle + \langle k' | U^p \frac{1}{E_k - H_o^p + i\varepsilon} U^p | \phi_k^+ \rangle . \quad (22)$$

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

$$T(k',k) = U^p(k',k) + \int \frac{dt}{(2\pi)^3} U^p(k',t) \frac{1}{E_k - E_t + i\varepsilon} T(t,k). \quad (23)$$

This equations must be solved either for model potentials (giving exact solutions) or numerically for the effective potential defined in (15a). In appendix 2 equation (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 $|\psi_k^+\rangle$ is more easily obtained transforming (19) back to the ket notation:

$$|\phi_k^+\rangle = |k\rangle - 4\pi \int \frac{dt}{(2\pi)^3} \frac{f(t,k)|t\rangle}{E_k - E_t + i\varepsilon} \quad (24)$$

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

$$|\psi_k^+\rangle = |k\rangle - \sum_{\bar{\alpha}} \langle \bar{\alpha}|k\rangle |\alpha\rangle - 4\pi \int \frac{dt}{(2\pi)^3} \frac{\dot{f}(k,t)|t\rangle}{E_k - E_t + i\varepsilon} +$$

$$+ 4\pi \sum_{\bar{\alpha}} |\bar{\alpha}\rangle \int \frac{dt}{(2\pi)^3} \frac{f(t,k)\langle \bar{\alpha}|t\rangle}{E_k - E_t + i\varepsilon} \quad (25)$$

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

$$\psi_k^+(r) = e^{ik \cdot r} - \sum_{\bar{\alpha}} \langle \bar{\alpha} | k \rangle \, \psi_{\bar{\alpha}}(r) - 4\pi \int \frac{dt}{(2\pi)^3} \frac{f(t,k)e^{it \cdot r}}{E_k - E_t + i\epsilon} +$$

$$+ \, 4\pi \sum_{\bar{\alpha}} \psi_{\bar{\alpha}}(r) \int \frac{dt}{(2\pi)^3} \frac{f(t,k) \langle \bar{\alpha} | t \rangle}{E_k - E_t + i\epsilon} . \tag{26}$$

From (26) it is clear that $\lim\limits_{\substack{U \to 0 \\ \bar{\alpha} \to \alpha}} \psi_k^+(r) = e^{ik \cdot r} - \sum_{\alpha} \langle \alpha | k \rangle \, \psi_\alpha(r)$ which is the pure metal true wave function.

e) Change In Electronic Density And Self-Consistency Problem

The solution of the scattering problem defined by equation (23) involves the self-consistent impurity potential U. As it was discussed below (cf. equations (6) and (7), given a charge difference Z, the potential U is defined through equation (7) self-consistently in terms of the U dependence of the charge density variation defined in (6). Now we obtain an explicit expression for $\Delta\rho(r)$, starting from the solution (26) of the scattering problem, which depends explicitly on U only through the transition probabilities f(k,k'). This calculation (cf. appendix 1 for details) shows that the change in electronic density is the sum of these terms:

$$\Delta\rho(r) = \sum_{k_{occ}} \Delta\rho_k(r) = \Delta\rho^{orth}(r) + \Delta\rho^{free}(r) + \Delta\rho^{free+orth}(r) \tag{27}$$

where these contributions are defined respectively as:

i) $\Delta\rho^{orth}(r) = 2\mathrm{Re}\sum_{k_{occ}} \left[e^{-ik\cdot r}\left\{ \sum_{\alpha} \psi_{\alpha}(r)\langle\alpha|k\rangle - \sum_{\alpha}\psi_{\bar\alpha}(r)\langle\bar\alpha|k\rangle \right\} \right]$

$+ \sum_{k_{occ}} \left[\sum_{\bar\alpha,\bar\alpha'} \psi_{\bar\alpha}(r)\psi_{\bar\alpha'}^{*}(r)\langle\bar\alpha|k\rangle\langle k|\bar\alpha'\rangle - \right.$

$\left. - \sum_{\alpha,\alpha'} \psi_{\alpha}(r)\psi_{\alpha'}^{*}(r)\langle\alpha|k\rangle\langle k|\alpha'\rangle \right]$ (28)

One notes that in the contribution $\Delta\rho^{orth}(r)$ 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 line of the periodic table.

ii) $\rho^{free}(r) = \sum \left\{ -2\mathrm{Re}\left[e^{-ik\cdot r}F(k,r) \right] + \left| F(k,r) \right|^2 \right\}$

where $F(k,r) = 4\pi \int \frac{dt}{(2\pi)^3} \frac{f(k,t)e^{itr}}{E_k - E_t + i\varepsilon}$. (29)

This "free electron" contributions corresponds formally to the
change in electronic density produced by the scattering of free
electrons by a potential which is defined through the transition
amplitudes $f(k,k')$.

iii) Finally, it remains the "interference terms" $\Delta\rho^{orth+free}(r)$
which describe how orthogonality requirements affect the scatter

ed free electron waves. This term is given by:

$$\Delta\rho^{free-orth}(r) = 2Re \sum_{k_{occ}} \left\{ \sum_{\bar{\alpha}} \psi_{\underline{\alpha}}(r)\bar{e}^{ikr} \langle \bar{\alpha}|F(k)\rangle \right\} +$$

$$+ 2Re \sum_{k_{occ}} \left\{ \sum_{\bar{\alpha}} \langle k|\bar{\alpha}\rangle \psi_{\underline{\alpha}}^{*}(r) F(k,r) \right\} -$$

$$- 2Re \sum_{k_{occ}} \left\{ \sum_{\bar{\alpha}} \psi_{\underline{\alpha}}(r)F^{*}(k,r)\langle \bar{\alpha}|F(k)\rangle \right\} -$$

$$- 2Re \sum_{k_{occ}} \left\{ \sum_{\bar{\alpha},\bar{\alpha}'} \langle k|\bar{\alpha}\rangle\psi_{\underline{\alpha}}^{*}(r) \psi_{\underline{\alpha}'}(r)\langle \bar{\alpha}'|F(k)\rangle \right\} +$$

$$+ \sum_{k_{occ}} \sum_{\bar{\alpha},\bar{\alpha}'} \psi_{\underline{\alpha}}(r)\psi_{\underline{\alpha}'}^{*}(r) \langle \bar{\alpha}|F(k)\rangle\langle F(k)|\bar{\alpha}'\rangle \qquad (30)$$

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

DISCUSSION

The equivalent problem described by equations (14-d) and (16) provides a very clear picture of node and charge effects. As it was discussed in the introduction, the usual description of normal metal based alloys corresponds to solve the scattering problem defined by a free electron gas and a potential

well, the depth of it being adjusted by the Friedel sum rule. In the picture developped here one still has a "free-electron like" scattering equation, but band effects are incorporated in the effective potential U^p defined by (14-b) and in the energy E_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 (14-d) contains two different terms, which are non-local, and correspond to the following:

i) The mixing potential $\sum_{\bar{\alpha}} \Delta(\lambda)|\bar{\alpha}\rangle\langle\bar{\alpha}| + \left\{ \sum_{\alpha} E_{\alpha}|\alpha\rangle\langle\alpha| - \sum_{\bar{\alpha}} E_{\bar{\alpha}}|\bar{\alpha}\rangle\langle\bar{\alpha}| \right\} - E_k \left\{ \sum_{\alpha}|\alpha\rangle\langle\alpha| - \sum_{\bar{\alpha}}|\bar{\alpha}\rangle\langle\bar{\alpha}| \right\}$ 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 have then 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 line of the periodic table (charge effects dominant) these terms may be neglected since $E_{\alpha} \cong E_{\bar{\alpha}}$ and $|\bar{\alpha}\rangle \cong |\alpha\rangle$.

ii) The "charge" and reaction potential $U(1-\sum_{\alpha}|\bar{\alpha}\rangle\langle\bar{\alpha}|)$ is just the self-consistent impurity potential U reduced by the factor $(1 - \sum_{\alpha}|\bar{\alpha}\rangle\langle\alpha|)$, 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 zero, and the existence of new closed

shells produces a non-vanishing 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 $U(1 - \sum_\alpha |\bar{\alpha}\rangle\langle\bar{\alpha}|)$ 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 $U(1-\sum|\bar{\alpha}\rangle\langle\bar{\alpha}|)$ has the meaning of a reaction potential.

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

APPENDIX 1
CALCULATION OF THE CHANGE IN ELECTRONIC DENSITY

In this appendix we evaluate expression (6) for $\Delta\rho(r)$ explicitly for $\psi_k(r)$ and $\psi_k^+(r)$ given respectively by expressions (2) and (26). The pure metal electronic density associated to wave vector k is given by:

$$|\psi_k(r)|^2 = (e^{-ik\cdot r} - \sum_\alpha \psi_\alpha^*(r)\langle k|\alpha\rangle)(e^{ik\cdot r} - \sum_\alpha \psi_\alpha(r)\langle\alpha|k\rangle)$$

$$|\psi_k(r)|^2 = 1 - 2Re\sum_\alpha e^{-ik\cdot r}\psi_\alpha(r)\langle\alpha|k\rangle + \sum_{\alpha,\alpha'} \psi_\alpha^*(r)\psi_{\alpha'}(r)\langle k|\alpha\rangle\langle\alpha'|k\rangle \qquad (A-1)$$

The alloy electronic density is then calculated from:

$$|\psi_k(r)|^2 = \left| e^{ik\cdot r} - \sum_{\bar{\alpha}}\langle\bar{\alpha}|k\rangle\psi_{\bar{\alpha}}(r) - 4\pi\int \frac{dt}{(2\pi)^3} \frac{f(t,k)e^{it\cdot r}}{E_k - E_t + i\varepsilon} + \right.$$

$$+ 4\pi \sum_{\bar{\alpha}} \psi_{\underline{\alpha}}(r) \left| \int \frac{dt}{(2\pi)^3} \frac{f(t,k)\langle\bar{\alpha}|t\rangle}{E_k - E_t + i\varepsilon} \right|^2 \quad (A-2)$$

From (A-2) one sees that three types of terms occur: firstly one has terms involving only orthogonality effects through the inner shell functions $\psi_{\underline{\alpha}}(r)$; secondly one has terms involving the transition probabilities, and these are "free electron like". Finally one has interference terms characterizing the orthogonality of scattered free electron waves to inner shell states. Now we evaluate explicitly (A-2) collecting the above mentioned terms:

$$|\psi_k^+(r)|^2 = 1 - 2\text{Re}\sum_{\bar{\alpha}} \langle\bar{\alpha}|k\rangle \, \psi_{\underline{\alpha}}(r) \, \bar{e}^{ik\cdot r} +$$

$$+ \sum_{\bar{\alpha},\bar{\alpha}'} \langle\bar{\alpha}|k\rangle \langle k|\bar{\alpha}'\rangle \, \psi_{\underline{\alpha}}(r) \psi_{\underline{\alpha}'}^*(r) - 8\pi \, \text{Re}\left[\bar{e}^{ik\cdot r} \int \frac{dt}{(2\pi)^3} \frac{f(t,k)e^{it\cdot r}}{E_k - E_t + i\varepsilon}\right] +$$

$$+ (4\pi)^2 \left| \int \frac{dt}{(2\pi)^3} \frac{f(t,k)e^{it\cdot r}}{E_k - E_t + i\varepsilon} \right|^2 +$$

$$+ 8\pi\text{Re}\sum_{\bar{\alpha}} \psi_{\underline{\alpha}}(r)\bar{e}^{ik\cdot r} \int \frac{dt}{(2\pi)^3} \frac{f(t,k)\langle\bar{\alpha}|t\rangle}{E_k - E_t + i\varepsilon} +$$

$$+ 8\pi\text{Re}\sum_{\bar{\alpha}} \langle k|\bar{\alpha}\rangle \psi_{\underline{\alpha}}^*(r) \int \frac{dt}{(2\pi)^3} \frac{f(t,k)e^{it\cdot r}}{E_k - E_t + i\varepsilon} -$$

$$- 8\pi\text{Re}\sum_{\bar{\alpha},\bar{\alpha}'} \langle k|\bar{\alpha}\rangle \psi_{\underline{\alpha}}^*(r) \, \psi_{\underline{\alpha}'}(r) \int \frac{dt}{(2\pi)^3} \frac{f(t,k)\langle\bar{\alpha}'|t\rangle}{E_k - E_t + i\varepsilon} +$$

$$+ (4\pi)^2 \sum_{\overline{\alpha},\overline{\alpha'}} \psi_{\overline{\alpha}}(r) \psi_{\overline{\alpha'}}^*(r) \int \frac{dt}{(2\pi)^3} \frac{f(t,k)\langle\overline{\alpha}|t\rangle}{E_k - E_t + i\epsilon}$$

$$\int \frac{dt'}{(2\pi)^3} \frac{f^*(t',k)\langle t'|\overline{\alpha'}\rangle}{E_k - E_{t'} - i\epsilon} -$$

$$- 2(4\pi)^2 \text{Re} \sum_{\overline{\alpha}} \psi_{\overline{\alpha}}(r) \int \frac{dt}{(2\pi)^3} \frac{f(t,k)\langle\overline{\alpha}|t\rangle}{E_k - E_t + i\epsilon} \int \frac{dt'}{(2\pi)^3} \frac{f^*(t',k)e^{it'\cdot r}}{E_k - E_{t'} - i\epsilon}$$

$$(A-3)$$

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

$$F(k,r) = 4\pi \int \frac{dt}{(2\pi)^3} \frac{f(t,k)e^{it\cdot r}}{E_k - E_t + i\epsilon} \qquad (A-4a)$$

and

$$|F(k)\rangle = 4\pi \int \frac{dt}{(2\pi)^3} \frac{f(t,k)|t\rangle}{E_k - E_t + i\epsilon} . \qquad (A-4b)$$

It follows then from (A-1) and (A-3) that the change in electronic density $\Delta\rho_k(r)$ is the sum of three contributions

$$\Delta\rho_k(r) = |\psi_k^+(r)|^2 - |\psi_k(r)|^2 = \Delta\rho_k^{orth}(r) + \Delta\rho_k^{free}(r) + \Delta\rho_k^{free+orth}(r)$$

$$(A-5a)$$

where

$$\Delta\rho_k^{orth}(r) = 2\text{Re}\left[e^{-ik\cdot r} \left\{\sum_{\alpha}\psi_\alpha(r)\langle\alpha|k\rangle - \sum_{\overline{\alpha}} \psi_{\overline{\alpha}}(r)\langle\overline{\alpha}|k\rangle\right\}\right]$$

$$+ \sum_{\overline{\alpha},\overline{\alpha'}} \psi_{\overline{\alpha}}(r)\psi_{\overline{\alpha'}}^*(r)\langle\overline{\alpha}|k\rangle\langle k|\overline{\alpha'}\rangle - \sum_{\alpha,\alpha'} \psi_\alpha(r)\psi_{\alpha'}^*(r)\langle\alpha|k\rangle\langle k|\alpha'\rangle$$

$$(A-5b)$$

$$\Delta\rho_k^{\text{free}}(r) = 2\text{Re}\left[\bar{e}^{ik\cdot r}\ F(k,r)\right] + |F(k,r)|^2 \qquad (A\text{-}5c)$$

$$\Delta\rho_k^{\text{free+orth}}(r) = 2\text{Re}\left\{\sum_{\bar{\alpha}}\psi_{\bar{\alpha}}(r)\bar{e}^{ik\cdot r}\langle\bar{\alpha}|F(k)\rangle\right\} +$$

$$+ 2\text{Re}\left\{\sum_{\bar{\alpha}}\langle k|\bar{\alpha}\rangle\psi_{\bar{\alpha}}^{*}(r)\ F(k,r)\right\} - 2\text{Re}\left\{\sum_{\bar{\alpha}}\psi_{\bar{\alpha}}(r)F^{*}(k,r)\langle\bar{\alpha}|F(k)\rangle\right\} -$$

$$- 2\text{Re}\left\{\sum_{\bar{\alpha},\bar{\alpha}'}\langle k|\bar{\alpha}\rangle\psi_{\bar{\alpha}}^{*}(r)\ \psi_{\bar{\alpha}'}(r)\langle\bar{\alpha}'|F(k)\rangle\right\} +$$

$$+ \sum_{\bar{\alpha},\bar{\alpha}'}\psi_{\bar{\alpha}}(r)\ \psi_{\bar{\alpha}'}^{*}(r)\langle\bar{\alpha}|F(k)\rangle\langle F(k)|\bar{\alpha}'\rangle \qquad (A\text{-}5d)$$

APPENDIX 2

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 equation (14d), and this approximate potential is called "model potential". The approximation consists in replacing the first term of (14d) by a **separable**, non local potential namely:

$$U(1-\sum_{\bar{\alpha}}|\bar{\alpha}\rangle\langle\bar{\alpha}|) \cong \sum_{\bar{\alpha}} A_{\bar{\alpha}}|\bar{\alpha}\rangle\langle\bar{\alpha}| \qquad (B\text{-}1)$$

where $A_{\bar{\alpha}}$ will be chosen in such a way that the self-consistency rule (6) is satisfied through equation (27). Since all the terms involved in (14d) are now of the form (B-1) we consider the following "model potential":

$$u^p = \sum_{\Gamma} A_{\Gamma} |\Gamma\rangle\langle\Gamma| \qquad \text{(B-2)}$$

$|\Gamma\rangle$ being "atomic like" states.

We introduce now the following notation:

$$\langle k|\Gamma\rangle = v_{\Gamma}(k) \qquad \text{(B-3a)}$$

$$\langle\Gamma|k'\rangle = v_{\Gamma}^{*}(k') \qquad \text{(B-3b)}$$

$$u^p(k',k) = \langle k'|u^p|k\rangle = \sum_{\Gamma} A_{\Gamma} v_{\Gamma}(k') v_{\Gamma}^{*}(k) \qquad \text{(B-3c)}$$

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

$$T(k',k) = \sum_{\Gamma} A_{\Gamma} v_{\Gamma}(k') v_{\Gamma}^{*}(k) + \sum_{\Gamma} A_{\Gamma} v_{\Gamma}(k') \cdot$$

$$\cdot \int \frac{dt}{(2\pi)^3} \frac{v_{\Gamma}^{*}(t) T(t,k)}{E_k - E_t + i\varepsilon} \qquad \text{(B-4)}$$

Introduce the auxiliary notation

$$x_{\Gamma}(k) = \int \frac{dt}{(2\pi)^3} \frac{v_{\Gamma}^{*}(t) T(t,k)}{E_k - E_t + i\varepsilon} \qquad \text{(B-5a)}$$

which gives for (B-4)

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

$$\text{(B-5b)}$$

From (B-5b) it is possible to derive a system of linear equations determining the $x_\Gamma(k)$; in fact multiplying (B-5b) by $\dfrac{v_{\Gamma_1}^*(k')}{E_k - E_{k'} + i\varepsilon}$ and summing over k' one gets:

$$\int \frac{dk'}{(2\pi)^3} \frac{v_{\Gamma_1}^*(k')T(k',k)}{E_k - E_{k'} + i\varepsilon} = \sum_\Gamma A_\Gamma v_\Gamma^*(k) \int \frac{dk'}{(2\pi)^3} \frac{v_{\Gamma_1}^*(k')v_\Gamma(k')}{E_k - E_{k'} + i\varepsilon} +$$

$$+ \sum_\Gamma A_\Gamma x_\Gamma(k) \int \frac{v_{\Gamma_1}^*(k')\, v_\Gamma(k')}{E_k - E_{k'} + i\varepsilon} \frac{dk'}{(2\pi)^3} \qquad \text{(B-6)}$$

which can be written as:

$$x_{\Gamma_1}(k) = B_{\Gamma_1}(k) + \sum_\Gamma A_{\Gamma\Gamma_1}(k)\, x_\Gamma(k) \qquad \text{(B-7)}$$

where

$$A_{\Gamma\Gamma_1}(k) = A_\Gamma \int \frac{dk'}{(2\pi)^3} \frac{v_{\Gamma_1}^*(k')\, v_\Gamma(k')}{E_k - E_{k'} + i\varepsilon} \qquad \text{(B-7)}$$

and

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

Equations (B-7) and (B-5b) provide the <u>exact</u> solutions for the T matrix.

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