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by

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ABSTRACT

Firstly, one discusses the effect of s-d hybridization in disordered transition metal alloys within the Coherent Potential Approximation (CPA), electron-electron correlations being described by Hubbard's approximation. The case of degenerate d bands hybridized with a s band is approximately solved within the Hartree-Fock scheme.

Secondly, pure transition metals including electron correlations and s-d hybridization are discussed within the CPA analogy, the consequences of alternative decouplings of the equations of motion for the propagators being investigated.

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INTRODUCTION

The coherent-potential approximation (CPA) has been largely used to provide a simple single-site description of disordered alloys [1, 2, 3]. In its simple form CPA describes only disordered alloys within the assumption of tight binding models for the conduction states.

A formulation of the CPA for transition metal alloys, within the Hartree-Fock scheme, was suggested by Brouers and Vedyayev [4] where s-d hybridization was taken into account. In this model, randomness occurs only within d states, the broad s band being assumed to correspond to the pure host. In all these works [1-4], a non-degenerate d band was always considered.

In a recent paper [5] the existence in transition metals of two t_{2g} and e_g d sub-bands was considered in order to describe the asphericity of the magnetic moments. Since in [5] the s band was completely ignored, it is the purpose of this work to suggest an approximate Hartree-Fock solution of the CPA problem involving the two d-character sub-bands in presence of hybridization with a broad s band. This calculation will be performed within the spirit of the works of Sadakata [6], Abito and Schweitzer [7], Esterling and Tahir-Kheli [8], namely the Green's function approach introduced by Zubarev [9]. The same approach is used to extend the results of Ref. 4 to the case of strong correlations in a non-degenerate d-band.

Another recent application of CPA procedures is the description of pure metals in presence of electron-electron correlation [10]. The central idea arises from the formulation of the alloy problem as presented by Shiba [11]. One describes the motion of the correlated electron by a spin- and energy- dependent effective self-energy Σ^{σ} which incorporates the effects of electron correlation. This self-energy is self-consistently determined by imposing that the scattering T-matrix associated to zero site, where the atom exhibits the full Coulomb correlation, vanishes, hence including Coulomb effects in this self-energy. The problem thus defined is solved[10] using the Green's function formalism, adopting the classical Hubbard's approach [12] and Roth's variational method [13]. In this paper we intend to include s-d mixing and to show that the simplest decoupling approximation for dealing with hybridization yields bad results and one must extend the equations of motion or trial operators in order to include mixing effects in the self-energy equation.

I. HYBRIDIZATION EFFECTS IN DISORDERED TRANSITION METAL ALLOYS

A) *STRONG CORRELATIONS IN A NON-DEGENERATE d BAND*

We consider the alloy system $A_x B_{1-x}$ described by a model Hamiltonian as proposed by Kishore and Joshi [14], including however diagonal disorder in the d band,

$$\mathcal{H} = \sum_{i\sigma} \varepsilon_i^{(d)} d_{i\sigma}^+ d_{i\sigma} + \sum_{ij\sigma} T_{ij}^{(d)} d_{i\sigma}^+ d_{j\sigma} + \sum_{ij\sigma} T_{ij}^{(s)} c_{i\sigma}^+ c_{j\sigma} +$$

$$+ \sum_{i} U_i^{(d)} n_{i\uparrow}^{(d)} n_{i\downarrow}^{(d)} + \sum_{ij\sigma} \{V_{sd}(R_i-R_j)\, c_{i\sigma}^+ d_{j\sigma} + V_{ds}(R_i-R_j) d_{i\sigma}^+ c_{j\sigma}\},\ n_{i\sigma}^{(d)}=d_{i\sigma}^+ d_{i\sigma}, \tag{1}$$

where $d_i\,(c_i)$ is the annihilation operator of a d(s) electron with spin $\sigma(\uparrow$ or $\downarrow)$ at the i-th Wannier site. The atomic d level $\varepsilon_i^{(d)}$ and the atomic Coulomb correlations $U_i^{(d)}$ may assume values $\varepsilon_A^{(d)}$ or $\varepsilon_B^{(d)}$ and $U_A^{(d)}$ and $U_B^{(d)}$ depending on whether the i-th site is occupied by an A or B atom with concentrations x and y = 1-x respectively. The other quantities as hopping integrals $T_{ij}^{(\lambda)}(\lambda = s,d)$ and mixing matrix elements V_{sd} or V_{ds} are assumed to be independent of the kind of atoms which occupy the i-th and j-th lattice site.

Following the method employed in Refs. 6, 7, 8 we firstly deduce the coupled equations of motion for the one-electron d-d propagator. Since Coulomb correlations are present and we intend to describe strong correlations, we adopt as our approximation scheme the classical Hubbard[12] decoupling. From equations (1) one easily derive the following exact coupled equations

$$(\omega-\varepsilon_i^{(d)})G_{ij\sigma}^{dd}(\omega) = \delta_{ij} + \sum_{\ell} T_{i\ell}^{(d)} G_{\ell j\sigma}^{dd}(\omega) + U_i^{(d)} G_{ij\sigma}^{dd,d}(\omega) + \sum_{\ell} V_{ds}(R_i-R_\ell)G_{\ell j\sigma}^{sd}(\omega) \tag{2a}$$

and

$$\omega\, G_{ij\sigma}^{sd}(\omega) = \sum_{\ell} T_{i\ell}^{(s)} G_{\ell j\sigma}^{sd}(\omega) + \sum_{\ell} V_{sd}(R_i-R_\ell)\, G_{\ell j\sigma}^{dd}(\omega) \tag{2b}$$

where

$$G_{ij\sigma}^{dd}(\omega) = \langle\langle d_{i\sigma}, d_{j\sigma}^{+}\rangle\rangle_\omega \; ; \quad G_{ij\sigma}^{dd,d}(\omega) = \langle\langle n_{i-\sigma}^{(d)} \, d_{i\sigma}; d_{j\sigma}^{+} \rangle\rangle_\omega \, .$$

In the limit of strong correlations ($U_i^{(d)} \to \infty$) and adopting Hubbard's procedure one verifies that the propagator $G_{ij\sigma}^{dd,d}(\omega)$ satisfies

$$\lim_{U_i^{(d)}\to\infty} U_i^{(d)} G_{ij\sigma}^{dd,d}(\omega) = - \delta_{ij} \langle n_{i-\sigma}^{(d)}\rangle - \langle n_{i-\sigma}^{(d)}\rangle \sum_{\ell} T_{i\ell}^{(d)} G_{\ell j\sigma}^{dd}(\omega) - \langle\Omega_{i-\sigma}\rangle G_{ij\sigma}^{dd}(\omega) - \langle n_{i-\sigma}^{(d)}\rangle \sum_{\ell} V_{ds}(R_i-R_\ell)\, G_{\ell j\sigma}^{sd}(\omega) \tag{3a}$$

In equation (3a), $\langle n_{i-\sigma}^{(d)}\rangle$ is the average d electron number with spin σ at the i-th site, while

$$\langle \Omega_{i-\sigma} \rangle = \langle S_{i-\sigma}\rangle + \langle V_{i-\sigma}\rangle, \tag{3b}$$

$\langle S_{i-\sigma}\rangle$ and $\langle V_{i-\sigma}\rangle$ being defined as

$$<S_{i-\sigma}> = \sum_{\ell} T_{i\ell}^{(d)} \{<d_{i-\sigma}^{+} d_{\ell-\sigma}> - <d_{\ell-\sigma}^{+} d_{i-\sigma}>\} , \qquad (3c)$$

$$<V_{i-\sigma}> = \sum_{\ell} \{V_{ds}(R_i-R_\ell) <d_{i-\sigma}^{+} c_{\ell-\sigma}> - V_{sd}(R_i-R_\ell) <c_{\ell-\sigma}^{+} d_{i-\sigma}>\} .$$

As it will be shown in the Appendix , the configuration-averaged quantity $<\Omega_{i-\sigma}>$ where the site i is occupied by an atom type A or B turns out to be zero, so in the following we neglect it. We want to emphasize that in obtaining (3) we have performed the decouplings

$$<<n_{i-\sigma}^{(d)} d_{\ell\sigma}; d_{j\sigma}^{+}>>_{\omega} \cong <n_{i-\sigma}^{(d)}> G_{\ell j\sigma}^{dd}(\omega) \qquad (4a)$$

$$<<n_{i-\sigma}^{(d)} c_{\ell\sigma}; d_{j\sigma}^{+}>>_{\omega} \cong <n_{i-\sigma}^{(d)}> G_{\ell j\sigma}^{sd}(\omega) \qquad (4b)$$

Later on (cf. Sec. II) we will see that in the CPA description of the pure hybridized and correlated metals the approximation (4b) leads to difficulties.

Equation (3a) together with (2a) and (2b) provides the following set of coupled equations

$$G_{ij\sigma}^{dd}(\omega) = \frac{1}{F_i^{\sigma}(\omega)} \{\delta_{ij} + \sum_{\ell} T_{i\ell}^{(d)} G_{\ell j\sigma}^{dd}(\omega) + \sum_{\ell} V_{ds}(R_i-R_\ell) G_{\ell j\sigma}^{sd}(\omega)\} \qquad (5a)$$

$$\omega G_{ij\sigma}^{sd}(\omega) = \sum_{\ell} T_{i\ell}^{(s)} G_{\ell j\sigma}^{sd}(\omega) + \sum_{\ell} V_{sd}(R_i-R_\ell) G_{\ell j\sigma}^{dd}(\omega) \qquad (5b)$$

where the locator $F_i^{\sigma}(\omega)$ is defined by

$$F_i^{\sigma}(\omega) = \frac{\omega - \varepsilon_i^{(d)}}{1 - <n_{i-\sigma}^{(d)}>} . \qquad (5c)$$

Now we follow strictly Ref. 6 suitably adapted to deal with mixing. From (5b) and Fourier transforming one has

$$G^{sd}_{kk'\sigma}(\omega) = \frac{V_{sd}(k)}{\omega - \varepsilon^{(s)}_k} G^{dd}_{kk'\sigma}(\omega) , \tag{6a}$$

or transforming back to Wannier representation

$$G^{sd}_{ij\sigma}(\omega) = \sum_{\ell} \left\{ \sum_{k} \frac{V_{sd}(k)}{\omega - \varepsilon^{(s)}_k} e^{-ik\cdot(R_i - R_\ell)} \right\} G^{dd}_{\ell j\sigma}(\omega) =$$

$$= \sum_{\ell} T^{mix}_{i\ell} G^{dd}_{\ell j\sigma}(\omega) , \tag{6b}$$

where we stress that $T^{mix}_{i\ell}$ do not involve any sort of disorder, and is in equal footing with the hopping $T^{(d)}_{i\ell}$. Defining

$$\tilde{T}^{(d)}_{i\ell} = T^{(d)}_{i\ell} + \sum_{m} V_{ds}(R_i - R_m) T^{mix}_{m\ell} , \tag{7a}$$

the final equation for the d-d propagator reads

$$G^{dd}_{ij\sigma}(\omega) = \frac{1}{F^{\sigma}_i(\omega)} \left\{ \delta_{ij} + \sum_{\ell} \tilde{T}^{(d)}_{i\ell} G^{dd}_{\ell j\sigma}(\omega) \right\} . \tag{7b}$$

Equation (7b) is formally identical to the starting equation of Ref. 6. The configuration averaged propagator (translationally invariant) is then defined by

$$\langle G^{dd}_{ij\sigma}(\omega)\rangle = \frac{1}{F^{\sigma}(\omega)} \left\{ \delta_{ij} + \sum_{\ell} \tilde{T}^{(d)}_{i\ell} \langle G^{dd}_{\ell j\sigma}(\omega)\rangle \right\}, \tag{8a}$$

which is solved by Fourier transformation to give

$$<G^{dd}_{ij\sigma}(\omega)> = \sum_k \frac{e^{ik\cdot(R_i-R_j)}}{F^{\sigma}(\omega) - \tilde{\varepsilon}^{(d)}_k} = <G^{dd}_{ji\sigma}(\omega)> \quad , \tag{8b}$$

with

$$\tilde{\varepsilon}^{(d)}_k = \varepsilon^{(d)}_k + \frac{|V_{sd}(k)|^2}{\omega - \varepsilon^{(s)}_k} \quad . \tag{8c}$$

The average locator $F^{\sigma}(\omega)$ should be self-consistently determined through the condition

$$x <G^{dd}_{ij\sigma}(\omega)>_{i=A} + y <G^{dd}_{ij\sigma}(\omega)>_{i=B} = <G^{dd}_{ij\sigma}(\omega)> \quad , \tag{9a}$$

where $<G^{dd}_{ij\sigma}(\omega)>_{i=A,B}$ is the averaged propagator for a medium where all atoms are described by the average locator $F^{\sigma}(\omega)$ except the atom at the site i which has $F^{\sigma}_i(\omega)$ as locator. These propagators satisfy [6]

$$<G^{dd}_{\ell j\sigma}(\omega)>_{i=A,B} = <G^{dd}_{\ell j\sigma}(\omega)>+<G^{dd}_{\ell i\sigma}(\omega)> \frac{F^{\sigma}(\omega) - F^{\sigma}_i(\omega)}{1-\left[F^{\sigma}(\omega)-F^{\sigma}_i(\omega)\right]<G^{dd}_{ii\sigma}(\omega)>} <G^{dd}_{ij\sigma}(\omega)> \quad . \tag{9b}$$

Consequently the self-consistency reads

$$x \frac{F^{\sigma}(\omega) - F^{\sigma}_A(\omega)}{1-\left[F^{\sigma}(\omega)-F^{\sigma}_A(\omega)\right]<G^{dd}_{ii\sigma}(\omega)>} + y \frac{F^{\sigma}(\omega) - F^{\sigma}_B(\omega)}{1-\left[F^{\sigma}(\omega)-F^{\sigma}_B(\omega)\right]<G^{dd}_{ii\sigma}(\omega)>} = 0 \tag{9c}$$

If one introduces a self-energy $\Sigma^{\sigma}(\omega)$ through

$$F^{\sigma}(\omega) = \omega - \Sigma^{\sigma}(\omega) \tag{10a}$$

and rewrites

$$F^{\sigma}_i(\omega) = \frac{\omega - \varepsilon^{(d)}_i}{1-<n^{(d)}_{i-\sigma}>} = \omega - \frac{\varepsilon^{(d)}_i - <n^{(d)}_{i-\sigma}>\omega}{1 - <n^{(d)}_{i-\sigma}>} = \omega - \tilde{\varepsilon}_{i\sigma}(\omega) \quad , \tag{10b}$$

the results (10) together with (9c) provide the final self-consistency relation determining the self-energy

$$\Sigma^{\sigma}(\omega) = x\,\tilde{\varepsilon}_{A\sigma}(\omega) + y\,\tilde{\varepsilon}_{B\sigma}(\omega) - \left[\tilde{\varepsilon}_{A\sigma}(\omega) - \Sigma^{\sigma}(\omega)\right] H^{\sigma}(\omega, \Sigma^{\sigma}(\omega)) \left[\tilde{\varepsilon}_{B\sigma}(\omega) - \Sigma^{\sigma}(\omega)\right] \tag{11a}$$

where

$$H^{\sigma}(\omega,\Sigma^{\sigma}(\omega)) = \langle G^{dd}_{ii\sigma}(\omega)\rangle = \sum_k \frac{1}{\omega - \tilde{\varepsilon}_k^{(d)} - \Sigma^{\sigma}(\omega)} = \sum_k \frac{1}{\omega - \varepsilon_k^{(d)} - \Sigma^{\sigma}(\omega) - \dfrac{|V_{sd}(k)|^2}{\omega - \varepsilon_k^{(s)}}} \tag{11b}$$

which is formally identical to Soven's result [1]. We note also that s-d mixing corrections enter in the C.P.A. condition in a quite similar way to Brouers and Vedyayev [4]. Finally one should remark the ω dependence in the "effective energies" $\tilde{\varepsilon}_{i\sigma}(\omega)$ due to the strong correlation treatment adopted here.

B) *APPROXIMATE HARTREE-FOCK SOLUTION FOR A DOUBLY DEGENERATE d BAND*

We start defining the adopted model Hamiltonian. The one-electron degenerate d band given by α and β sub-bands is written in the Wannier representation as

$$\mathcal{H}_d = \sum_{i\sigma} \varepsilon_i^{(\alpha)}\, \alpha_i^{(\alpha)}\, \alpha^{+}_{i\sigma}\, \alpha_{i\sigma} + \sum_{ij\sigma} T_{ij}^{(\alpha)}\, \alpha^{+}_{i\sigma}\, \alpha_{j\sigma} + \sum_{i\sigma} \varepsilon_i^{(\beta)}\, \beta^{+}_{i\sigma}\, \beta_{i\sigma} + \sum_{ij\sigma} T_{ij}^{(\beta)} \beta^{+}_{i\sigma} \beta_{j\sigma} \tag{12a}$$

where $\varepsilon_i^{(\alpha)}$, $\varepsilon_i^{(\beta)}$ are the random energies associated to the atoms A and B, and $T_{ij}^{(\lambda)}$ ($\lambda = \alpha$ or β) do not involve disorder.

The doubly degenerate d band superposes to a broad s band

$$\mathcal{H}_s = \sum_{ij\sigma} T_{ij}^{(s)}\, c^{+}_{i\sigma}\, c_{j\sigma} \tag{12b}$$

where $T_{ij}^{(s)}$ involves no disorder at all. These bands hybridize through the following term

$$\mathcal{H}_{sd} = \sum_{ij\sigma} \left\{ V_{sd}^{(\alpha)}(R_i - R_j)\; c_{i\sigma}^{+}\; \alpha_{j\sigma} + V_{ds}^{(\alpha)}(R_i - R_j)\; \alpha_{i\sigma}^{+}\; c_{j\sigma} \right\} +$$

$$+ \sum_{ij\sigma} \left\{ V_{sd}^{(\beta)}(R_i - R_j)\; c_{i\sigma}^{+}\; \beta_{j\sigma} + V_{ds}^{(\beta)}(R_i - R_j)\; \beta_{i\sigma}^{+}\; c_{j\sigma} \right\} . \qquad (12c)$$

The Coulomb correlations are present through

$$\mathcal{H}_{dd} = \sum_i U_i^{(\alpha)}\, n_{i\uparrow}^{(\alpha)}\, n_{i\downarrow}^{(\alpha)} + \sum_i U_i^{(\beta)}\, n_{i\uparrow}^{(\beta)}\, n_{i\downarrow}^{(\beta)} + \sum_i U_i^{\alpha\beta} \left\{ n_{i\uparrow}^{(\alpha)}\, n_{i\downarrow}^{(\beta)} + n_{i\uparrow}^{(\beta)} n_{i\downarrow}^{(\alpha)} \right\} +$$

$$+ \sum_{i\sigma} \left(U_i^{\alpha\beta} - J_i^{\alpha\beta} \right) n_{i\sigma}^{(\alpha)}\; n_{i\sigma}^{(\beta)} \qquad (12d)$$

Due to degeneracy now we have, contrary to case (I.A), simultaneous presence of Coulomb and exchange interactions. The complete Hamiltonian is then

$$\mathcal{H} = \mathcal{H}_d + \mathcal{H}_s + \mathcal{H}_{sd} + \mathcal{H}_{dd} \qquad (13)$$

Next we write the equations of motion for the α-α propagator. Using the Hartree-Fock scheme and defining Hartree-Fock renormalized energies as

$$E_{i\sigma}^{(\alpha)} = \varepsilon_i^{(\alpha)} + U_i^{(\alpha)} \langle n_{i-\sigma}^{(\alpha)} \rangle + U_i^{\alpha\beta} \langle n_{i-\sigma}^{(\beta)} \rangle + \left(U_i^{\alpha\beta} - J_i^{\alpha\beta} \right) \langle n_{i\sigma}^{(\beta)} \rangle , \qquad (14)$$

(a similar equation holds for $E_{i\sigma}^{(\beta)}$ just changing α by β where it appears) one gets the following coupled equations of motion (in matrix form)

$$\left[\omega \hat{I} - \hat{E}^{(\alpha)} - \hat{T}^{(\alpha)} \right] \cdot \hat{G}^{\alpha\alpha}(\omega) = \hat{I} + \hat{V}_{ds}^{(\alpha)} \cdot \hat{G}^{s\alpha}(\omega) , \qquad (15a)$$

$$\left[\omega \hat{I} - \hat{T}^{(s)} \right] \cdot \hat{G}^{s\alpha}(\omega) = \hat{V}_{sd}^{(\alpha)} \cdot \hat{G}^{\alpha\alpha}(\omega) + \hat{V}_{sd}^{(\beta)} \cdot \hat{G}^{\beta\alpha}(\omega) , \qquad (15b)$$

$$\left[\omega \hat{I} - \hat{E}^{(\beta)} - \hat{T}^{(\beta)} \right] \cdot \hat{G}^{\beta\alpha}(\omega) = \hat{V}_{ds}^{(\beta)} \cdot \hat{G}^{s\alpha}(\omega) \qquad (15c)$$

where we introduced the Hartree-Fock energy matrices $\left[\hat{E}^{(\lambda)}\right]_{ij} = E_{i\sigma}^{(\lambda)}\,\delta_{ij}$, $(\lambda = \alpha,\beta)$, the hopping matrices $\left[\hat{T}^{(\lambda)}\right]_{ij} = T_{ij}^{(\lambda)}$ $(\lambda = \alpha,\beta)$ and the mixing matrices $\left[\hat{V}_{sd}^{(\lambda)}\right]_{ij} = V_{sd}^{(\lambda)}\,(R_i - R_j)$. Combining equations (15c) and (15b) one gets for $\hat{G}^{\beta\alpha}(\omega)$

$$\hat{G}^{\beta\alpha}(\omega) = \left[\omega\hat{I} - \hat{E}^{(\beta)} - \hat{\tilde{T}}^{(\beta)}\right]^{-1} \cdot \hat{V}_{ds}^{(\beta)} \cdot \left[\omega\hat{I} - \hat{T}^{(s)}\right]^{-1} \cdot \hat{V}_{sd}^{(\alpha)} \cdot \hat{G}^{\alpha\alpha}(\omega) \quad (16a)$$

where the effective hopping matrix $\hat{\tilde{T}}^{(\beta)}$ is defined as

$$\hat{\tilde{T}}^{(\beta)} = \hat{T}^{(\beta)} + \hat{V}_{ds}^{(\beta)} \cdot \left[\omega\hat{I} - \hat{T}^{(s)}\right]^{-1} \cdot \hat{V}_{sd}^{(\beta)} \quad . \quad (16b)$$

Using the result (16a) in equation (15b) one gets for $\hat{V}_{ds}^{(\alpha)} \cdot \hat{G}^{s\alpha}(\omega)$, which is the quantity one needs to determine to substitute in (15a)

$$\hat{V}_{ds}^{(\alpha)} \cdot \hat{G}^{s\alpha}(\omega) = \hat{V}_{ds}^{(\alpha)} \cdot \left[\omega\hat{I} - \hat{T}^{(s)}\right]^{-1} \cdot \hat{V}_{sd}^{(\alpha)} \cdot \hat{G}^{\alpha\alpha}(\omega) +$$

$$+ \hat{V}_{ds}^{(\alpha)} \cdot \left[\omega\hat{I} - \hat{T}^{(s)}\right]^{-1} \cdot \hat{V}_{sd}^{(\beta)} \cdot \left[\omega\hat{I} - \hat{E}^{(\beta)} - \hat{\tilde{T}}^{(\beta)}\right]^{-1} \cdot \hat{V}_{ds}^{(\beta)} \cdot \left[\omega\hat{I} - \hat{T}^{(s)}\right]^{-1} \cdot \hat{V}_{sd}^{(\alpha)} \cdot \hat{G}^{\alpha\alpha}(\omega) \quad (17)$$

Equation (17) suggests the simplest way to deal with this intricate problem. Since simultaneous disorder cannot be fully discussed using a simple procedure, we use the fact that the last term which incorporates the simultaneous disorder in the α and β sub-bands exists only due to a repeated hybridization with the common s band, i.e., the term which involves the disorder in the β sub-band is proportional, at least, to the fourth order in mixing. If we neglect this term, one obtains simply

$$\hat{V}_{ds}^{(\alpha)} \cdot \hat{G}^{s\alpha}(\omega) \cong \hat{V}_{ds}^{(\alpha)} \cdot \left[\omega\hat{I} - \hat{T}^{(s)}\right]^{-1} \cdot \hat{V}_{sd}^{(\alpha)} \cdot \hat{G}^{\alpha\alpha}(\omega) \quad . \quad (18)$$

We emphasize that the above result just corresponds to ignore the only possible process (which is a (at least) fourth order process) by which an α electron can see the disorder in the β sub-band. Adopting (18) as our main approximation and combining with (15a) one gets

$$\left\{\omega\hat{I} - \hat{E}^{(\alpha)} - \hat{T}^{(\alpha)} - \hat{V}^{(\alpha)}_{ds} \cdot \left[\omega\hat{I} - \hat{T}^{(s)}\right]^{-1} \cdot \hat{V}^{(\alpha)}_{sd}\right\} \cdot \hat{G}^{\alpha\alpha}(\omega) = \hat{I} \quad (19a)$$

or in Wannier representation

$$(\omega - E^{(\alpha)}_{i\sigma})\, G^{\alpha\alpha}_{ij\sigma}(\omega) = \delta_{ij} + \sum_{\ell} \tilde{T}^{(\alpha)}_{i\ell}\, G^{\alpha\alpha}_{\ell j\sigma}(\omega) \quad (19b)$$

$\tilde{T}^{(\alpha)}_{i\ell}$ being

$$\tilde{T}^{(\alpha)}_{i\ell} = T^{(\alpha)}_{i\ell} + T^{mix}_{i\ell}\,, \qquad T^{mix}_{i\ell} = \sum_{k} V^{(\alpha)}_{ds}(k)\, \frac{e^{-ik\cdot(R_i - R_\ell)}}{\omega - \varepsilon^{(s)}_k}\, V^{(\alpha)}_{sd}(k)\,. \quad (19c)$$

Equation (19b) is formally identical to the result obtained in Ref. 4 with an essential difference. The renormalized Hartree-Fock energies include the effects of disorder within the β sub-band as introduced in Ref. 5. Consequently the asphericity of the alloy magnetic moments is also present in this formulation with the extra improvement of considering s-d hybridization. To summarize: the approximation embodied in (18) consists in considering the s band as a source of hybridization independently for the α and β states. Finally the problem defined by (19b) is formally identical to the previous case discussed in equation (7b) with the new locator defined as

$$\frac{1}{F^{(\alpha)}_{i\sigma}(\omega)} = \frac{1}{\omega - E^{(\alpha)}_{i\sigma}} \quad (19d)$$

s-d mixing effects being incorporated in the new $H^{\sigma}_{(\alpha)}(\omega)$ which now turns out to be

$$< G^{\alpha\alpha}_{ii\sigma}(\omega)> = H^{\sigma}_{(\alpha)}(\omega) = \sum_{k} \frac{}{\omega - \varepsilon^{(\alpha)}_k - \Sigma^{\sigma}_{(\alpha)} - \dfrac{|V^{(\alpha)}_{sd}(k)|^2}{\omega - \varepsilon^{(s)}_k}}\,. \quad (19e)$$

Expression (19e) generalizes the result obtained in Ref.5 to include s-d hybridization in the simplest possible way.

II. HYBRIDIZATION EFFECTS IN INTERACTING PURE TRANSITION METALS

The Hamiltonian we adopt to describe pure transition metals is

$$\mathcal{H} = \sum_{ij\sigma} T_{ij}^{(s)} C_{i\sigma}^{+} C_{j\sigma} + \sum_{ij} T_{ij}^{(d)} d_{i\sigma}^{+} d_{j\sigma} + U \sum_{i} n_{i\uparrow}^{(d)} n_{i\downarrow}^{(d)} + \sum_{ij\sigma} \left\{ V_{sd}(R_i - R_j) \, c_{i\sigma}^{+} d_{j\sigma} + V_{ds}(R_i - R_j) \, d_{i\sigma}^{+} c_{j\sigma} \right\}. \qquad (20)$$

We follow strictly Roth's suggestion [10] of describing correlation effects through a CPA procedure starting from the following effective Hamiltonian

$$\mathcal{H}_{eff} = \sum_{ij\sigma} T_{ij}^{(s)} c_{i\sigma}^{+} c_{j\sigma} + \sum_{ij\sigma} T_{ij}^{(d)} d_{i\sigma}^{+} d_{j\sigma} + \sum_{i\sigma} n_{i\sigma}^{(d)} \Sigma^{\sigma} + \sum_{ij\sigma} \left\{ V_{sd} (R_i - R_j) \, c_{i\sigma}^{+} d_{j\sigma} + V_{ds}(R_i - R_j) d_{i\sigma}^{+} c_{j\sigma} \right\} + U \, n_{o\uparrow}^{(d)} \, n_{o\downarrow}^{(d)} - \sum_{\sigma} n_{o\sigma}^{(d)} \Sigma^{\sigma}, \qquad (21)$$

where Σ^{σ} is the effective self-energy describing correlation effects. We recall that the main spirit of the method consists to replace a translationally invariant problem as defined in (20) by an alloy problem where the origin incorporates the full Coulomb correlation. The effective Hamiltonian (21) still includes the difficulty of dealing with the Coulomb intra-atomic term at the origin and we intend to discuss this problem in two approximations, namely Hubbard's approach [12, 15] and briefly repport the results of using Roth's variational method [13].

A) DISCUSSION OF HUBBARD'S DECOUPLING PROCEDURE

We use the Green's function method [8] and obtain

$$\omega \, G_{ij\sigma}^{dd}(\omega) = \delta_{ij} + \sum_{\ell} T_{i\ell}^{(d)} \, G_{\ell j\sigma}^{dd}(\omega) + \Sigma^{\sigma} \, G_{ij\sigma}^{dd}(\omega) + \sum_{\ell} V_{ds}(R_i - R_\ell) G_{\ell j\sigma}^{sd}(\omega) + \delta_{io} \left[U \, G_{oj\sigma}^{dd,d}(\omega) - \Sigma^{\sigma} \, G_{oj\sigma}^{dd}(\omega) \right]. \qquad (22a)$$

The propagator $G^{sd}_{ij\sigma}(\omega)$ satisfies the exact equation of motion

$$\omega\, G^{sd}_{ij\sigma}(\omega) = \sum_{\ell} T^{(s)}_{i\ell}\, G^{sd}_{\ell j\sigma}(\omega) + \sum_{\ell} V_{sd}(R_i - R_\ell)\, G^{dd}_{\ell j\sigma}(\omega)\,. \tag{22b}$$

Let us determine the propagator $G^{dd,d}_{oj\sigma}(\omega)$ generated by the Coulomb correlation at the origin. Before doing the calculation we note that if Hartree-Fock decoupling is performed ($G^{dd,d}_{oj\sigma}(\omega) \cong \langle n^{(d)}_{o-\sigma}\rangle\; G^{dd}_{oj\sigma}(\omega)$) one obtains the expected result $\sum^{\sigma} = U\; \langle n^{(d)}_{o-\sigma}\rangle$ at the end of the calculations. Physically, this just means that in the Hartree-Fock scheme the electrons move in the effective field generated by opposite spin electrons. We obtain $U\, G^{dd,d}_{oj\sigma}(\omega)$ from the equation of motion for the propagator $\Gamma^{dd}_{ij\sigma}(\omega) = \langle\langle n^{(d)}_{o-\sigma}\; d_{i\sigma};\, d^{+}_{j\sigma}\rangle\rangle_\omega$ just taking i = 0; then $\Gamma^{dd}_{oj\sigma}(\omega) = G^{dd,d}_{oj\sigma}(\omega)$. One gets

$$\begin{aligned}
\omega\, \Gamma^{dd}_{ij\sigma}(\omega) = {} & \langle n^{(d)}_{o-\sigma}\rangle \delta_{ij} + \textstyle\sum^{\sigma} \Gamma^{dd}_{ij\sigma}(\omega) + \sum_{\ell} T^{(d)}_{i\ell}\, \Gamma^{dd}_{\ell j\sigma}(\omega) + \\
& + \sum_{\ell} T^{(d)}_{o\ell}\, \langle\langle \left[d^{+}_{o-\sigma}\, d_{\ell-\sigma} - d^{+}_{\ell-\sigma}\, d_{o-\sigma} \right] d_{i\sigma};\, d^{+}_{j\sigma} \rangle\rangle_\omega + \\
& + \sum_{\ell} V_{ds}(R_i - R_\ell)\, \langle\langle n^{(d)}_{o-\sigma}\; c_{\ell\sigma};\, d^{+}_{j\sigma}\rangle\rangle_\omega + \Bigg\{ \sum_{\ell} V_{ds}(-R_\ell) \langle\langle d^{+}_{o-\sigma}\, c_{\ell-\sigma} d_{i\sigma};\, d^{+}_{j\sigma}\rangle\rangle_\omega \\
& - \sum_{\ell} V_{sd}(-R_\ell)\, \langle\langle c^{+}_{\ell-\sigma}\, d_{o-\sigma}\, d_{i\sigma};\, d^{+}_{j\sigma}\rangle\rangle_\omega \Bigg\} + \delta_{io}(U - \textstyle\sum^{\sigma})\, G^{dd,d}_{oj\sigma}(\omega).
\end{aligned} \tag{23}$$

Equation (23) still involves complicated propagators and we may introduce the simplification of neglecting the "broadening correction" [15], namely

$$\begin{aligned}
& \sum_{\ell} T^{(d)}_{o\ell} \langle\langle \left[d^{+}_{o-\sigma}\, d_{\ell-\sigma} - d^{+}_{\ell-\sigma}\, d_{o-\sigma} \right] d_{i\sigma};\, d^{+}_{j\sigma}\rangle\rangle_\omega \cong \\
& \cong \left\{ \sum_{\ell} T^{(d)}_{o\ell} \left[\langle d^{+}_{o-\sigma}\, d_{\ell-\sigma}\rangle - \langle d^{+}_{\ell-\sigma}\, d_{o-\sigma}\rangle \right] \right\} G^{dd}_{ij\sigma}(\omega)
\end{aligned} \tag{24a}$$

and

$$\sum_\ell V_{ds}(-R_\ell)\langle\langle d^+_{o-\sigma}\, c_{\ell-\sigma}\, d_{i\sigma};\, d^+_{j\sigma}\rangle\rangle_\omega - \sum_\ell V_{sd}(-R_\ell)\langle\langle c^+_{\ell-\sigma}\, d_{o-\sigma}\, c_{i\sigma};\, d^+_{j\sigma}\rangle\rangle_\omega \cong$$

$$\cong \left\{ \sum_\ell V_{ds}(-R_\ell)\, \langle d^+_{o-\sigma}\, c_{\ell-\sigma}\rangle - \sum_\ell V_{sd}(-R_\ell)\, \langle c^+_{\ell-\sigma}\, d_{o-\sigma}\rangle \right\} G^{dd}_{ij\sigma}(\omega) \;. \qquad (24b)$$

Since the involved correlation functions will be calculated after imposing the T-matrix associated to scattering at the origin to vanish, one sees that translational invariance is restored. So, the right hand side of (24) vanishes also. Then one is faced with the equation

$$\omega\, \Gamma^{dd}_{ij\sigma}(\omega) \cong \langle n^{(d)}_{o-\sigma}\rangle\, \delta_{ij} + \textstyle\sum^\sigma \Gamma^{dd}_{ij\sigma}(\omega) + \sum_\ell T^{(d)}_{i\ell}\; \Gamma^{dd}_{\ell j\sigma}(\omega) +$$

$$+ \sum_\ell\; V_{ds}(R_i-R_\ell)\, \langle\langle n^{(d)}_{o-\sigma}\;\; c_{\ell\sigma};\, d^+_{j\sigma}\rangle\rangle_\omega + \delta_{io}\, (U-\textstyle\sum^\sigma)\; G^{dd,d}_{oj\sigma}(\omega). \qquad (25)$$

At this point some remarks about (25) are necessary. The first one is that due to the special form of the propagator $\Gamma^{dd}_{ij\sigma}(\omega)$, which involves only $n^{(d)}_{o-\sigma}$, one is not obliged to perform the usual Hubbard's approximation [12] in the $T^{(d)}_{i\ell}$ term of (25). This means that the "scattering correction" [15] is already included in the formalism [10]. Secondly, the effect of s-d hybridization is to generate a new function $\langle\langle n^{(d)}_{o-\sigma}\;\; c_{\ell\sigma};\, d^+_{j\sigma}\rangle\rangle_\omega$. The simplest approach, which was adopted in Sec. I-A of this work (see equation 4) is to decouple this propagator according to

$$\langle\langle\, n^{(d)}_{o-\sigma}\;\; c_{\ell\sigma};\, d^+_{j\sigma}\,\rangle\rangle_\omega \cong \langle n^{(d)}_{o-\sigma}\rangle\; \langle\langle c_{\ell\sigma};\, d^+_{j\sigma}\rangle\rangle_\omega \;. \qquad (26)$$

Hence, one obtains the following first form for the equation of motion determining $\Gamma^{dd}_{ij\sigma}(\omega)$

$$\omega\, \Gamma^{dd}_{ij\sigma}(\omega) \cong \langle n^{(d)}_{o-\sigma}\rangle\, \delta_{ij} + \textstyle\sum^\sigma \Gamma^{dd}_{ij\sigma}(\omega) + \sum_\ell T^{(d)}_{i\ell}\, \Gamma^{dd}_{\ell j\sigma}(\omega) +$$

$$+ \langle n^{(d)}_{o-\sigma}\rangle \sum_\ell V_{ds}(R_i-R_\ell)\; G^{sd}_{\ell j\sigma}(\omega) + \;\delta_{io}(U - \textstyle\sum^\sigma)\; G^{dd,d}_{oj\sigma}(\omega) \qquad (27)$$

An alternative procedure is to write an equation of motion for the propagator $<<n^{(d)}_{o-\sigma}\; c_{i\sigma};\, d^{+}_{j\sigma}>>_{\omega}$ which is simple, due to its special form. One gets

$$\omega <<n^{(d)}_{o-\sigma}\; c_{i\sigma};\, d^{+}_{j\sigma}>>_{\omega} = \sum_{\ell} T^{(s)}_{i\ell} << n^{(d)}_{o-\sigma}\; c_{\ell\sigma};\, d^{+}_{j\sigma} >>_{\omega} + \sum_{\ell} T^{(d)}_{o\ell}\left\{<<d^{+}_{o-\sigma}\, d_{\ell-\sigma}\, c_{i\sigma};\, d^{+}_{j\sigma}>>_{\omega} - <<d^{+}_{\ell-\sigma}\, d_{o-\sigma}\, c_{i\sigma};\, d^{+}_{j\sigma}>>_{\omega}\right\} + \sum_{\ell} V_{sd}(R_i-R_\ell)\Gamma^{dd}_{\ell j\sigma}(\omega) + \sum_{\ell}\left\{V_{ds}(-R_\ell)<<d^{+}_{o-\sigma}\, c_{\ell-\sigma}\, c_{i\sigma};\, d^{+}_{j\sigma}>>_{\omega} - V_{sd}(-R_\ell)<<c^{+}_{\ell-\sigma}\, d_{o-\sigma}\, c_{i\sigma};\, d^{+}_{j\sigma}>>_{\omega}\right\} \quad (28a)$$

Again neglecting "broadening corrections" one obtains similarly to (24)

$$\omega<<n^{(d)}_{o-\sigma}\; c_{i\sigma};\, d^{+}_{j\sigma}>>_{\omega} = \sum_{\ell} T^{(s)}_{i\ell} << n^{(d)}_{o-\sigma}\; c_{\ell\sigma};\, d^{+}_{j\sigma} >>_{\omega} + \sum_{\ell} V_{sd}(R_i-R_\ell)\Gamma^{dd}_{\ell j\sigma}(\omega) \quad (28b)$$

which Fourier transformed gives

$$<< n^{(d)}_{o-\sigma}\; c_{k\sigma};\, d^{+}_{k'\sigma}>>_{\omega} = \frac{1}{\omega - \varepsilon^{(s)}_{k}} V_{sd}(k)\; \Gamma^{dd}_{kk'\sigma}(\omega) \quad (28c)$$

or transformed back to Wannier representation

$$<<n^{(d)}_{o-\sigma}\, c_{i\sigma};\, d^{+}_{j\sigma}>>_{\omega} = \sum_{\ell} T^{mix}_{i\ell}\; \Gamma^{dd}_{\ell j\sigma}(\omega) \;, \quad (28d)$$

where

$$T^{mix}_{i\ell} = \sum_{k} \frac{V_{sd}(k)}{\omega-\varepsilon^{(s)}_{k}}\, e^{-ik\cdot(R_i-R_\ell)} \;.$$

Expression (28d) provides the second alternative equation for $\Gamma^{dd}_{ij\sigma}(\omega)$, namely

$$\omega\,\Gamma^{dd}_{ij\sigma}(\omega)=\langle n^{(d)}_{0-\sigma}\rangle\delta_{ij}+\textstyle\sum^{\sigma}\Gamma^{dd}_{ij\sigma}(\omega)+\sum_{\ell}T^{(d)}_{i\ell}\Gamma^{dd}_{\ell j\sigma}(\omega)+\sum_{\ell m}V_{ds}(R_i-R_\ell)T^{mix}_{\ell m}\Gamma^{dd}_{mj\sigma}(\omega)\,+$$

$$+\,\delta_{io}(U-\textstyle\sum^{\sigma})G^{dd,d}_{oj\sigma}(\omega)\;. \qquad (29)$$

Next, we solve explicitly the problem defined by (22a), (22b) and (27) or (29). We start from the second case defined by equation (29). Fourier transforming (22a), (22b) and (29)

$$(\omega-\varepsilon^{(d)}_k-\textstyle\sum^{\sigma})G^{dd}_{kk'\sigma}(\omega)=\delta_{kk'}+V_{ds}(k)G^{sd}_{kk'\sigma}(\omega)+U\,\gamma^{dd}_{k'\sigma}(\omega)-\sum^{\sigma}\Theta^{dd}_{k'\sigma}(\omega), \qquad (30a)$$

$$(\omega-\varepsilon^{(s)}_k)\,G^{sd}_{kk'\sigma}(\omega)=V_{sd}(k)\,G^{dd}_{kk'\sigma}(\omega) \qquad (30b)$$

and

$$\left(\omega-\varepsilon^{(d)}_k-\textstyle\sum^{\sigma}-\dfrac{|V_{sd}(k)|^2}{\omega-\varepsilon^{(s)}_k}\right)\Gamma^{dd}_{kk'\sigma}(\omega)=\langle n^{(d)}_{0-\sigma}\rangle\;\delta_{kk'}+(U-\textstyle\sum^{\sigma})\;\gamma^{dd}_{k'\sigma}(\omega) \qquad (30c)$$

where we denoted

$$\Theta^{dd}_{k'\sigma}(\omega)=\sum_{k''}G^{dd}_{k''k'\sigma}(\omega)\qquad\text{and}\qquad\gamma^{dd}_{k'\sigma}(\omega)=\sum_{k''}\Gamma^{dd}_{k''k'\sigma}(\omega)\;.$$

Combining (30a) and (30b), one has

$$\left\{\omega-\varepsilon^{(d)}_k-\textstyle\sum^{\sigma}-\dfrac{|V_{sd}(k)|^2}{\omega-\varepsilon^{(s)}_k}\right\}G^{dd}_{kk'\sigma}(\omega)=\delta_{kk'}+U\,\gamma^{dd}_{k'\sigma}(\omega)-\textstyle\sum^{\sigma}\Theta^{dd}_{k'\sigma}(\omega)\;. \qquad (30d)$$

which exhibits the same structure of (30c).

Equations (30c) and (30d) define a scattering problem which is easily solved. Introducing

$$\tilde{\varepsilon}^{(d)}_k=\varepsilon^{(d)}_k+\frac{|V_{sd}(k)|^2}{\omega-\varepsilon^{(s)}_k}$$

and defining the function $F^{\sigma}(\omega)$, (which generalizes Roth's [10] F^{σ} function)

$$F^{\sigma}(\omega) = \sum_k \frac{1}{\omega - \varepsilon_k^{(d)} - \dfrac{|V_{sd}(k)|^2}{\omega - \varepsilon_k^{(s)}} - \Sigma^{\sigma}} ,$$

one gets from (30c) and (30d) summing over k

$$\gamma^{dd}_{k'\sigma}(\omega) = \frac{\langle n^{(d)}_{o-\sigma}\rangle}{\omega - \tilde{\varepsilon}^{(d)}_{k'} - \Sigma^{\sigma}} + (U - \Sigma^{\sigma})\, F^{\sigma}(\omega)\, \gamma^{dd}_{k'\sigma}(\omega) \tag{31a}$$

and

$$\theta^{dd}_{k'\sigma}(\omega) = \frac{1}{\omega - \tilde{\varepsilon}^{(d)}_{k'} - \Sigma^{\sigma}} + U\, F^{\sigma}(\omega)\, \gamma^{dd}_{k'\sigma}(\omega) - \Sigma^{\sigma}\, F^{\sigma}(\omega)\, \theta^{dd}_{k'\sigma}(\omega) \; . \tag{31b}$$

From equations (31) we easily obtain $\gamma^{dd}_{k'\sigma}(\omega)$ and $\theta^{dd}_{k'\sigma}(\omega)$ determining completely the propagator $G^{dd}_{kk'\sigma}(\omega)$. The final result is then

$$G^{dd}_{kk'\sigma}(\omega) = \frac{\delta_{kk'}}{\omega - \tilde{\varepsilon}^{(d)}_{k} - \Sigma^{\sigma}} + \frac{1}{\omega - \tilde{\varepsilon}^{(d)}_{k} - \Sigma^{\sigma}}\, T^{\sigma}(\omega, \Sigma^{\sigma})\, \frac{1}{\omega - \tilde{\varepsilon}^{(d)}_{k'} - \Sigma^{\sigma}} , \tag{32a}$$

where the T-matrix is

$$T^{\sigma}(\omega, \Sigma^{\sigma}) = \frac{U \langle n^{(d)}_{o-\sigma}\rangle - \Sigma^{\sigma} + \Sigma^{\sigma}(U - \Sigma^{\sigma})\, F^{\sigma}(\omega)}{\left[1 - (U - \Sigma^{\sigma})\, F^{\sigma}(\omega)\right]\left[1 + \Sigma^{\sigma}\, F^{\sigma}(\omega)\right]} \tag{32b}$$

Hence, the condition $T^{\sigma}(\omega, \Sigma^{\sigma}) = 0$ determining self-consistently the self-energy which generalizes Roth's result[10] is

$$\Sigma^{\sigma} = U\langle n_{o-\sigma}^{(d)}\rangle + (U - \Sigma^{\sigma})\, F^{\sigma}(\omega, \Sigma^{\sigma})\, \Sigma^{\sigma} \quad . \tag{33}$$

Now we consider the first alternative (equation 27) involving the decoupling of the Green's function generated by the mixing. The coupled system (using equation (30d) and equation 27) Fourier transformed, is

$$(\omega - \tilde{\varepsilon}_k^{(d)} - \Sigma^{\sigma}) G_{kk'\sigma}^{dd}(\omega) = \delta_{kk'} + U\gamma_{k'\sigma}^{dd}(\omega) - \Sigma^{\sigma}\theta_{k'\sigma}^{dd}(\omega) \quad , \tag{34a}$$

$$(\omega-\varepsilon_k^{(d)} - \Sigma^{\sigma})\, \Gamma_{kk'\sigma}^{dd}(\omega) = \langle n_{o-\sigma}^{(d)}\rangle\, \delta_{kk'} + \langle n_{o-\sigma}^{(d)}\rangle\, V_{ds}(k)\, G_{kk'\sigma}^{sd}(\omega) + (U - \Sigma^{\sigma})\, \gamma_{k'\sigma}^{dd}(\omega) \tag{34b}$$

and

$$(\omega - \varepsilon_k^{(s)})\, G_{kk'\sigma}^{sd}(\omega) = V_{sd}(k)\, G_{kk'\sigma}^{dd}(\omega). \tag{34c}$$

From (34c) and (34b) one gets

$$(\omega-\varepsilon_k^{(d)} - \Sigma^{\sigma})\, \Gamma_{kk'\sigma}^{dd}(\omega) = \langle n_{o-\sigma}^{(d)}\rangle\delta_{kk'} + \frac{\langle n_{o-\sigma}^{(d)}\rangle |V_{sd}(k)|^2}{\omega - \varepsilon_k^{(s)}}\, G_{kk'\sigma}^{dd}(\omega) + (U-\Sigma^{\sigma})\, \gamma_{k'\sigma}^{dd}(\omega) \tag{34d}$$

Equations (34 a) and (34d) must now be solved simultaneously for $\gamma_{k'\sigma}^{dd}(\omega)$ and $\theta_{k'\sigma}^{dd}(\omega)$. Substituting (34a) in (34d), performing the sum over k and the corresponding algebra to obtain the $\gamma_{k'\sigma}^{dd}(\omega)$ and $\theta_{k'\sigma}^{dd}(\omega)$ unknowns, one finally has

$$G^{dd}_{kk'\sigma}(\omega) = \frac{\delta_{kk'}}{\omega-\tilde{\varepsilon}^{(d)}_k - \Sigma^\sigma} + \frac{1}{\omega-\tilde{\varepsilon}^{(d)}_k - \Sigma^\sigma} T^\sigma_1(\omega, \Sigma^\sigma) \frac{1}{\omega- \tilde{\varepsilon}^{(d)}_{k'} - \Sigma^\sigma} \tag{35a}$$

the T-matrix being now

$$T^\sigma_1(\omega, \Sigma^\sigma) = \frac{U\langle n^{(d)}_{o-\sigma}\rangle - \Sigma^\sigma + \Sigma^\sigma(U - \Sigma^\sigma) F^\sigma_1(\omega)}{(1 + \Sigma^\sigma F_\sigma(\omega)) \left[1 - F^\sigma_1(\omega)(U - \Sigma^\sigma)\right] + U\langle n^{(d)}_{o-\sigma}\rangle (F^\sigma_1(\omega) - F^\sigma(\omega))}, \tag{35b}$$

where $F^\sigma(\omega)$ has been defined previously and $F^\sigma_1(\omega)$ is defined by

$$F^\sigma_1(\omega) = \sum_k \frac{1}{\omega - \varepsilon^{(d)}_k - \Sigma^\sigma} \tag{35c}$$

Then, the self-consistency condition becomes

$$\Sigma^\sigma = U\langle n^{(d)}_{o-\sigma}\rangle + \Sigma^\sigma F^\sigma_1(\omega, \Sigma^\sigma)(U - \Sigma^\sigma). \tag{36}$$

The puzzling result contained in (36) is that the mixing V_{sd} is completely absent, so the condition for magnetic instability is the same of Roth's paper[10]. The decoupling (26) thus *completely screens the effect of mixing in the determination of the self-energy.* We intend now to discuss in more detail the implications of the decoupling (26). To do that we firstly consider equation (34b) which is rewritten as

$$(\omega - \tilde{\varepsilon}^{(d)}_k - \Sigma^\sigma)\,\Gamma^{dd}_{kk'\sigma}(\omega) = \langle n^{(d)}_{o-\sigma}\rangle\,\delta_{kk'} + (U - \Sigma^\sigma)\,\gamma^{dd}_{k'\sigma}(\omega) -$$

$$- \left\{ \frac{|V_{sd}(k)|^2}{\omega - \varepsilon^{(s)}_k}\,\Gamma^{dd}_{kk'\sigma}(\omega) - \langle n^{(d)}_{o-\sigma}\rangle\,V_{ds}(k)\,G^{sd}_{kk'\sigma}(\omega) \right\} \tag{37}$$

where we have summed and subtracted

$$\frac{|V_{sd}(k)|^2}{\omega - \varepsilon_k^{(s)}} \; \Gamma^{dd}_{kk'\sigma}(\omega) \; .$$

The purpose of this trick is to transform the last term of (37) in a "scattering correction form" in Hubbard's sense [15]. In fact, we can use the exact result (28c), (except for "broadening corrections" neglected here)

$$\left\{ \frac{|V_{sd}(k)|^2}{\omega - \varepsilon_k^{(s)}} \Gamma^{dd}_{kk'\sigma}(\omega) - \langle n^{(d)}_{o-\sigma}\rangle V_{ds}(k)\, G^{sd}_{kk'\sigma}(\omega) \right\} = V_{ds}(k) \left\{ \langle\langle n^{(d)}_{o-\sigma}\, c_{k\sigma};\, d^{+}_{k'\sigma}\rangle\rangle_{\omega} - \right.$$

$$\left. - \langle n^{(d)}_{o-\sigma}\rangle \langle\langle c_{k\sigma};\, d^{+}_{k'\sigma}\rangle\rangle_{\omega} \right\} = V_{ds}(k) \left[\langle\langle (n^{(d)}_{o-\sigma} - \langle n^{(d)}_{o-\sigma}\rangle) c_{i\sigma};\, d^{+}_{j\sigma}\rangle\rangle_{\omega} \right]_{kk'} \qquad (38)$$

Then the final result is

$$(\omega - \tilde{\varepsilon}^{(d)}_k - \Sigma^{\sigma})\, \Gamma^{dd}_{kk'\sigma}(\omega) = \langle n^{(d)}_{o-\sigma}\rangle \delta_{kk'} + (U - \Sigma^{\sigma})\, \gamma^{dd}_{k'\sigma}(\omega) \; -$$

$$- V_{ds}(k) \left[\langle\langle (n^{(d)}_{o-\sigma} - \langle n^{(d)}_{o-\sigma}\rangle)\, c_{i\sigma};\, d^{+}_{j\sigma}\rangle\rangle_{\omega} \right]_{kk'} \qquad (39)$$

Comparison between (39) and (30c) shows that through the decoupling (26) it still remains in the equation of motion for $\Gamma^{dd}_{kk'\sigma}(\omega)$ a scattering correction-like term associated to s-d hybridization, a spurious term in this formulation, which should include all scattering corrections from the beginning [10].

B) ROTH'S VARIATIONAL METHOD: SUMMARY OF THE RESULTS

In this paragraph we quote the results of the application of Roth's variational method[13] to the effective Hamiltonian (21). In the case of a pure d band, as discussed in Ref. 10, the basis set of operators is $\{d_{i\sigma}, n^{(d)}_{o-\sigma}\, d_{i\sigma}\}$, where one must note that, contrary to the usual case, instead of $n^{(d)}_{i-\sigma}\, d_{i\sigma}$ one considers the correlation operator only at the site where Coulomb interaction exists, namely at the origin. We recall also that the main result obtained in Ref. 10 is that equation (36) still holds if in the definition of $F^{\sigma}_{1}(\omega)$ a band shift is introduced, namely

$$F^{\sigma}_{1}(\omega) = \sum_{k} \frac{1}{\omega - \varepsilon^{(d)}_{k} - W_{k-\sigma} - \Sigma^{\sigma}} \tag{40a}$$

If one intends to generalize this calculation to the effective Hamiltonian (21), thus including s-d hybridization, one is tempted to replace the above trial operators by the following set: $\{c_{i\sigma};\, d_{i\sigma};\, n^{(d)}_{o-\sigma}\, d_{i\sigma}\}$. Once the calculation is performed one verifies that again the self-consistency condition is (36), with $F^{\sigma}_{1}(\omega)$ defined exactly by expression (40a), *without* the effect of mixing, except for a contribution in the band-shift. In order to include properly mixing effects one needs to enlarge the basis set to include the operator $n^{(d)}_{o-\sigma}\, c_{i\sigma}$ generated by s-d hybridization. The result is essentially equal to (33), but now with a s-d corrected band-shift, and it reads

$$F^{\sigma}(\omega) = \sum_{k} \frac{1}{\omega - \tilde{\varepsilon}^{(d)}_{k} - \tilde{W}_{k-\sigma} - \Sigma^{\sigma}} \;. \tag{40-b}$$

Thus, Roth's approximation provides also an example of the difficulties associated to hybridization and shows that only in the enlarged basis set s-d renormalization effects in (36) are present. The details of this calculation and the application of the variational method to deal with disordered alloys is the subject of a forthcoming paper.

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APPENDIX: CALCULATION OF THE CONFIGURATION AVERAGED FUNCTION $<\Omega_{i-\sigma}>$

We recall from the text that

$$<\Omega_{i-\sigma}> = \sum_{\ell} T_{i\ell}^{(d)} \left\{ <d_{i-\sigma}^{+} d_{\ell-\sigma}> - <d_{\ell-\sigma}^{+} d_{i-\sigma}> \right\} + \sum_{\ell} \left\{ V_{ds}(R_i - R_\ell) <d_{i-\sigma}^{+} c_{\ell-\sigma}> - V_{sd}(R_i - R_\ell) <c_{\ell-\sigma}^{+} d_{i-\sigma}> \right\} . \quad \text{(A-1)}$$

In this expression the site i is occupied by an atom type A or B, so the correlation functions should be derived from the results obtained for averaged propagators where the atom at site i is a given one. We start with the simplest case, namely the first term of (A-1). The d-d propagator is

$$<G_{\ell j\sigma}^{dd}(\omega)>_i = <G_{\ell j\sigma}^{dd}(\omega)> + <G_{\ell i\sigma}^{dd}(\omega)> \frac{F^{\sigma}(\omega) - F_i^{\sigma}(\omega)}{1 - \left[F^{\sigma}(\omega) - F_i^{\sigma}(\omega)\right] <G_{ii\sigma}^{dd}(\omega)>} <G_{ij\sigma}^{dd}(\omega)>. \quad \text{(A-2)}$$

Specializing the sites ℓ, j one has

$$<G_{\ell i\sigma}^{dd}(\omega)>_i = <G_{\ell i\sigma}^{dd}(\omega)> \left\{ 1 + \frac{\left[F^{\sigma}(\omega) - F_i^{\sigma}(\omega)\right] <G_{ii\sigma}^{dd}(\omega)>}{1 - \left[F^{\sigma}(\omega) - F_i^{\sigma}(\omega)\right] <G_{ii\sigma}^{dd}(\omega)>} \right\} = \frac{<G_{\ell i\sigma}^{dd}(\omega)>}{1 - \left[F^{\sigma}(\omega) - F_i^{\sigma}(\omega)\right] <G_{ii\sigma}^{dd}(\omega)>} \quad \text{(A-3a)}$$

$$<G_{i\ell\sigma}^{dd}(\omega)>_i = <G_{i\ell\sigma}^{dd}(\omega)> \left\{ 1 + \frac{\left[F^{\sigma}(\omega) - F_i^{\sigma}(\omega)\right] <G_{ii\sigma}^{dd}(\omega)>}{1 - \left[F^{\sigma}(\omega) - F_i^{\sigma}(\omega)\right] <G_{ii\sigma}^{dd}(\omega)>} \right\} = \frac{<G_{\ell i\sigma}^{dd}(\omega)>}{1 - \left[F^{\sigma}(\omega) - F_i^{\sigma}(\omega)\right] <G_{ii\sigma}^{dd}(\omega)>} =$$

$$= <G_{\ell i\sigma}^{dd}(\omega)>_i \quad \text{(A-3b)}$$

where we have used equation (8b) of the text. Hence, the first term reads

$$\sum_{\ell} T_{i\ell}^{(d)}\left\{<d_{i-\sigma}^{+}\, d_{\ell-\sigma}>-<d_{\ell-\sigma}^{+}\, d_{i-\sigma}>\right\} = \sum_{\ell} T_{i\ell}^{(d)}\left\{\mathcal{F}_{\omega}\left[<G_{\ell i\sigma}^{dd}(\omega)>_{i}\right] - \mathcal{F}_{\omega}\left[<G_{i\ell\sigma}^{dd}(\omega)>_{i}\right]\right\} = 0, \tag{A-4}$$

where $\mathcal{F}_{\omega}$ is as usual [15]

$$\mathcal{F}_{\omega}\left[G_{ij\sigma}(\omega)\right] = \frac{i}{2\pi}\int_{-\infty}^{+\infty} d\omega\; f(\omega)\left[G_{ij\sigma}(\omega+i\delta)-G_{ij\sigma}(\omega-i\delta)\right],$$ $\delta \to 0$ and $f(\omega)$ being the Fermi function.

From (A-1) one has then

$$<\Omega_{i-\sigma}>= \sum_{\ell}\left\{V_{ds}(R_i-R_{\ell})\,\mathcal{F}_{\omega}\left[<G_{\ell i\sigma}^{sd}(\omega)>_{i}\right] - V_{sd}(R_i-R_{\ell})\,\mathcal{F}_{\omega}\left[<G_{i\ell\sigma}^{ds}(\omega)>_{i}\right]\right\}. \tag{A-5}$$

In order to calculate these averaged propagators in presence of an atom type A in site i, we start from a Dyson-like equation

$$G = <G> + <G>\, VG\,, \tag{A-6}$$

where $<G>$ is the configuration averaged propagator and V is the localized potential at site i, given by $|i,d>\, V_i\, <i,\, d|$. From (A-6) one has the following s-d and d-s matrix elements of (A-6)

$$<G_{\ell j\sigma}^{sd}(\omega)>_{i} = <G_{\ell j\sigma}^{sd}(\omega)> + <G_{\ell i\sigma}^{sd}(\omega)>\, V_i\, <G_{ij\sigma}^{dd}(\omega)>_{i} \tag{A-7a}$$

and

$$<G_{\ell j\sigma}^{ds}(\omega)>_{i} = <G_{\ell j\sigma}^{ds}(\omega)> + <G_{\ell i\sigma}^{dd}(\omega)>\, V_i\, <G_{ij\sigma}^{ds}(\omega)>_{i}\,, \tag{A-7b}$$

with $V_i = F^{\sigma}(\omega) - F_i^{\sigma}(\omega)$.

Equation (A-7a) is solved, remembering equation (9b) of the text

$$<G_{\ell j\sigma}^{dd}(\omega)>_{i} = <G_{\ell j\sigma}^{dd}(\omega)> + <G_{\ell i\sigma}^{dd}(\omega)>\,\frac{F^{\sigma}(\omega) - F_i^{\sigma}(\omega)}{1-\left[F^{\sigma}(\omega)-F_i^{\sigma}(\omega)\right]<G_{ii\sigma}^{dd}(\omega)>}\,<G_{ij\sigma}^{dd}(\omega)>$$

which specialized for $\ell = i$ gives

$$<G^{dd}_{ij\sigma}(\omega)>_i = \frac{<G^{dd}_{ij\sigma}(\omega)>}{1-\left[F^{\sigma}(\omega)-F^{\sigma}_i(\omega)\right]<G^{dd}_{ii\sigma}(\omega)>},$$

So the solution of (A-7a) is

$$<G^{sd}_{\ell j\sigma}(\omega)>_i = <G^{sd}_{\ell j\sigma}(\omega)> + <G^{sd}_{\ell i\sigma}(\omega)> \frac{F^{\sigma}(\omega) - F^{\sigma}_i(\omega)}{1-\left[F^{\sigma}(\omega)-F^{\sigma}_i(\omega)\right]<G^{dd}_{ii\sigma}(\omega)>} <G^{dd}_{ij\sigma}(\omega)>. \quad \text{(A-8)}$$

Equation (A-7b) is solved taking firstly $\ell = i$. One has

$$\left\{1 - \left[F^{\sigma}(\omega) - F^{\sigma}_i(\omega)\right] <G^{dd}_{ii\sigma}(\omega)> \right\} <G^{ds}_{ij\sigma}(\omega)>_i = <G^{ds}_{ij\sigma}(\omega)>,$$

Then

$$<G^{ds}_{\ell j\sigma}(\omega)>_i = <G^{ds}_{\ell j\sigma}(\omega)> + <G^{dd}_{\ell i\sigma}(\omega)> \frac{F^{\sigma}(\omega) - F^{\sigma}_i(\omega)}{1-\left[F^{\sigma}(\omega)-F^{\sigma}_i(\omega)\right]<G^{dd}_{ii\sigma}(\omega)>} <G^{ds}_{ij\sigma}(\omega)>. \quad \text{(A-9)}$$

Now we use the solutions (A-9) and (A-8) to compute the value of (A-5). Taking $j=i$ in (A-8) one has

$$<G^{sd}_{\ell i\sigma}(\omega)>_i = \frac{<G^{sd}_{\ell i\sigma}(\omega)>}{1-\left[F^{\sigma}(\omega)-F^{\sigma}_i(\omega)\right]<G^{dd}_{ii\sigma}(\omega)>}. \quad \text{(A-10a)}$$

Similarly, taking $\ell = i$ and $j = \ell$ in (A-9) one gets

$$<G^{ds}_{i\ell\sigma}(\omega)>_i = \frac{<G^{ds}_{i\ell\sigma}>}{1-\left[F^{\sigma}(\omega)-F^{\sigma}_i(\omega)\right]<G^{dd}_{ii\sigma}(\omega)>} \quad \text{(A-10b)}$$

It remains to compute the configuration averaged propagators $<G^{sd}_{\ell i\sigma}(\omega)>$ and $<G^{ds}_{i\ell\sigma}(\omega)>$. From equation (6b) of the text one has

$$<G^{sd}_{ij\sigma}(\omega)>_k = (T^{mix}_{ij})_k <G^{dd}_{ij\sigma}(\omega)>_k = \frac{V_{sd}(k)}{\omega - \varepsilon^{(s)}_k} \frac{1}{F^{\sigma}(\omega) - \tilde{\varepsilon}^{(d)}_k},$$

so

$$\langle G^{sd}_{ij\sigma}(\omega)\rangle_k = \frac{V_{sd}(k)}{(\omega-\varepsilon^{(s)}_k)(F^{\sigma}(\omega)-\varepsilon^{(d)}_k)-|V_{sd}(k)|^2} = V_{sd}(k)\, L_k(\omega) \quad . \qquad \text{(A-11)}$$

Now we calculate explicitly the propagator $\langle G^{ds}_{ij\sigma}(\omega)\rangle_k$.

The equations of motion for the propagator $G^{ds}_{ij\sigma}(\omega)$ are

$$(\omega-\varepsilon^{(d)}_i)G^{ds}_{ij\sigma}(\omega) = \sum_{\ell} T^{(d)}_{i\ell}\; G^{ds}_{\ell j\sigma}(\omega) + U_d\, G^{dd,s}_{ij\sigma}(\omega) + \sum_{\ell} V_{ds}(R_i-R_\ell)\; G^{ss}_{\ell j\sigma}(\omega) \;, \qquad \text{(A-12a)}$$

$$\omega\, G^{ss}_{ij\sigma}(\omega) = \delta_{ij} + \sum_{\ell} T^{(s)}_{i\ell}\; G^{ss}_{\ell j\sigma}(\omega) + \sum_{\ell} V_{sd}(R_i-R_\ell)\; G^{ds}_{\ell j\sigma}(\omega) \;, \qquad \text{(A-12b)}$$

$$\lim_{U_d\to\infty} U_d\, G^{dd,s}_{ij\sigma}(\omega) = -\,\langle n^{(d)}_{i-\sigma}\rangle \sum_{\ell} T^{(d)}_{i\ell}\; G^{ds}_{\ell j\sigma}(\omega) - \langle \Omega_{i-\sigma}\rangle\, G^{ds}_{ij\sigma}(\omega) -$$

$$-\,\langle n^{(d)}_{i-\sigma}\rangle \sum_{\ell} V_{ds}(R_i-R_\ell)\; G^{ss}_{\ell j\sigma}(\omega) \;, \qquad \text{(A-12c)}$$

the usual Hubbard decoupling being used to derive (A-12c).

From (A-12a) and (A-12c) one gets

$$G^{ds}_{ij\sigma}(\omega) = \frac{1}{F^{\sigma}_i(\omega)} \left\{ \sum_{\ell} T^{(d)}_{i\ell}\;\; G^{ds}_{\ell j\sigma}(\omega) + \sum_{\ell} V_{ds}(R_i-R_\ell)\; G^{ss}_{\ell j\sigma}(\omega) \right\} , \qquad \text{(A-13)}$$

where $F^{\sigma}_i(\omega)$ is defined in equation (5c). Fourier transforming (A-12b) and configuration averaging one obtains

$$\langle G^{ss}_{ij\sigma}(\omega)\rangle_k = \frac{1}{\omega-\varepsilon^{(s)}_k} + \frac{V_{sd}(k)}{\omega-\varepsilon^{(s)}_k}\; \langle G^{ds}_{ij\sigma}(\omega)\rangle_k \qquad \text{(A-14a)}$$

and from (A-13)

$$\left[F^{\sigma}(\omega) - \varepsilon^{(d)}_k\right] \;\langle G^{ds}_{ij\sigma}(\omega)\rangle_k = V_{ds}(k)\, \langle G^{ss}_{ij\sigma}(\omega)\rangle_k \quad . \qquad \text{(A-14b)}$$

Finally, from (A-14) it follows that

$$\langle G^{ds}_{ij\sigma}(\omega)\rangle_k = \frac{V_{ds}(k)}{(\omega-\varepsilon^{(s)}_k)(F^{\sigma}(\omega)-\varepsilon^{(d)}_k)-|V_{sd}(k)|^2} = V_{ds}(k)\, L_k(\omega) \quad . \qquad \text{(A-15)}$$

Now we compute the first term of (A-5). Using (A-11) and (A-10a) one arrives to

$$\sum_{\ell} V_{ds}(R_i-R_\ell)\,\mathcal{F}_\omega\left[\langle G^{sd}_{\ell i\sigma}(\omega)\rangle_i\right] = \mathcal{F}_\omega\left\{\sum_k \frac{|V_{sd}(k)|^2 L_k(\omega)}{1-\left[F^\sigma(\omega)-F^\sigma_i(\omega)\right]\langle G^{dd}_{ii\sigma}(\omega)\rangle}\right\}. \quad \text{(A-16a)}$$

Similarly, using (A-15) and (A-10b), the second term of (A-5) reads

$$\sum_{\ell} V_{sd}(R_i-R_\ell)\,\mathcal{F}_\omega\left[\langle G^{ds}_{i\ell\sigma}(\omega)\rangle_i\right] = \mathcal{F}_\omega\left\{\sum_k \frac{|V_{sd}(k)|^2\, L_k(\omega)}{1-\left[F^\sigma(\omega)-F^\sigma_i(\omega)\right]\langle G^{dd}_{ii\sigma}(\omega)\rangle}\right\}. \quad \text{(A-16b)}$$

Consequently

$$\langle \Omega_{i-\sigma} \rangle \equiv 0\,.$$