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REMARKS ON THE ELECTRONIC STRUCUTRE AND ELECTRON CORRELATIONS IN ACTINIDES

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INTRODUCTION

The electronic structure and magnetic properties of actinide metals has has been the subject of several works in recent years [1, 2]. One of the most interesting feature of these metals is the absence of magnetism in the beginning of the series in contrast with the almost similar series of the rare-earth metals. Characterized by an incomplete 5f shell which is gradually filled along the series, they differ from the rare-earth metals in two fundamental aspects. Firstly due the spatial extension of the 5f shell, one expects in solids the existence of f-bands instead of the usual atomic-like f states typical of rare-earth metals. Secondly

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the existence of a d-band (also shown to exist in rare-earths) which is expected to be larger in energy in actinides by spatial extension arguments, seems to play a fundamental role in the properties of actinide metals. In fact, a recent work by R. Jullien et al.[2] has shown that the magnetic properties of actinide metals can be explained by assuming a strong d-f hybridization among 5f and 6d states. We adopt here the same point of view as in [2], and treat the d-f hybridization matrix element as a phenomenological parameter, without any ambition of calculating it from first principles. It is the purpose of this work to extend ref. 2 in two points. Firstly, instead of assuming two virtual bound states (f and d) we consider two bands of f and d type (f is assumed to be a narrow band). Within this picture we expect to recover the real situation of rather important overlap among neighbouring 5f shells. Secondly, electron-electron correlations discussed in ref.2 within the Hartree-Fock approximation are discussed here within the variational method of Roth[3]. This method has proven to be satisfying in discussing electron correlations in narrow bands, and has been applied to s-d hybridized bands in transition metals by the authors[4] and by Faulkner and Schweitzer[5]. In this paper the results obtained in ref. 4 are generalized to the case of two hybridized f and d bands. This paper is organized as follows: firstly we discuss the case of hybridized bands in presence of intra atomic f and d Coulomb repulsion and compare with the Hubbard approximation.[6] Secondly the case of inter-orbital (d-f) Coulomb interaction is discussed and compared to the previous case. Finally the method of Kishore and Joshi [8] is discussed to obtain analytical expressions for the density of states and the self-consistency is briefly discussed.

II. FORMULATION OF THE PROBLEM AND INTRA ORBITAL REPULSION CASE

The general formulation of the actinide metal problem would envolve an Hamiltonian describing three overlapping bands (of s, d and f character) hybridization among them (through V_{sd}, V_{sf} and V_{df} matrix elements) and the Coulomb repulsion terms. Previous experience [8] with the Hartree-Fock approximation as applied to this band picture show that the most interesting effects in the electronic density of states are associated to the V_{df} matrix elements. Although not necessary but for simplicity reasons we omit here the s-like band which introduce only the usual effects of s-d and s-f hybridization, and consider the following model hamiltonian for actinide metals; in second quantized form and in the Wannier representation:

$$\mathcal{H} = \sum_{i,j,\sigma} T_{ij}^{(d)} d_{i\sigma}^{+} d_{j\sigma} + \sum_{i,j,\sigma} T_{ij}^{(f)} f_{i\sigma}^{+} f_{j\sigma} + U_f \Sigma_i n_{i\uparrow}^{(f)} n_{i\downarrow}^{(f)} +$$

$$+ U_d \Sigma_i n_{i\uparrow}^{(d)} n_{i\downarrow}^{(d)} + U_{df} \sum_i \left\{ n_{i\uparrow}^{(d)} n_{i\downarrow}^{(f)} + n_{i\downarrow}^{(d)} n_{i\uparrow}^{(f)} \right\} + \sum_{i,\sigma} \left\{ V_{df} d_{i\sigma}^{+} f_{i\sigma} + \right.$$

$$\left. + V_{fd} f_{i\sigma}^{+} d_{i\sigma} \right\} \qquad (1)$$

In expression (1) the two first terms describe the energy bands of d and f character respectively, the third and fourth terms the intra orbital Coulomb interactions, the last two terms being the inter orbital Coulomb interaction and the f-d hybridization terms. However in this first part we drop the inter orbital term, the effect of it being separately discussed in the third part. In this part we consider the following hamiltonian:

$$\mathcal{H} = \sum_{i,j,\sigma} T_{ij}^{(d)} d_{i\sigma}^{+} d_{j\sigma} + \sum_{i,j,\sigma} T_{ij}^{(f)} f_{i\sigma}^{+} f_{j\sigma} + \sum_{i,\sigma} \left\{ V_{df} d_{i\sigma}^{+} f_{i\sigma} + \right.$$

$$\left. + V_{fd} f_{i\sigma}^{+} d_{i\sigma} \right\} + U_d \sum_i n_{i\uparrow}^{(d)} n_{i\downarrow}^{(d)} + U_f \sum_i n_{i\uparrow}^{(f)} n_{i\downarrow}^{(f)} \qquad (2)$$

It is important to emphasize that the hamiltonian without the last two terms is exactly soluble, the difficulty lying in the Coulomb terms.

Now we follow strictly Roth's procedure [3].

By analogy to his choice we take the following basis set:

$$\left\{ d_{i\sigma};\ n_{i-\sigma}^{(d)} d_{i\sigma};\ f_{i\sigma};\ n_{i-\sigma}^{(f)} f_{i\sigma} \right\} \qquad (3)$$

In the absence of Coulomb repulsion ($U_d = U_f = 0$) the first and the third term of this basis set provides the exact solution of the problem. Now the operators of the basis set satisfy the following equations of motion:

$$\left[d_{i\sigma}, \mathcal{H} \right] = \Sigma_{\ell} T_{i\ell}^{(d)} d_{\ell\sigma} + U_d n_{i-\sigma}^{(d)} d_{i\sigma} + V_{df} f_{i\sigma} \qquad \text{(4-a)}$$

$$\left[n_{i-\sigma}^{(d)} d_{i\sigma}, \mathcal{H} \right] = U_d n_{i-\sigma}^{(d)} d_{i\sigma} + \Sigma_{\ell} T_{i\ell}^{(d)} \left\{ n_{i-\sigma}^{(d)} d_{\ell\sigma} + d_{i-\sigma}^{+} d_{\ell-\sigma} d_{i\sigma} - \right.$$

$$\left. - d_{\ell-\sigma}^{+} d_{i-\sigma} d_{i\sigma} \right\} + V_{df} \left\{ n_{i-\sigma}^{(d)} f_{i\sigma} + d_{i-\sigma}^{+} f_{i-\sigma} d_{i\sigma} - f_{i-\sigma}^{+} d_{i-\sigma} d_{i\sigma} \right\} \text{(4-b)}$$

$$\left[f_{i\sigma}, \mathcal{H}\right] = \Sigma_\ell \, T^{(f)}_{i\ell} \, f_{\ell\sigma} + U_f \, n^{(f)}_{i-\sigma} \, f_{i\sigma} + V_{fd} \, d_{i\sigma} \tag{4-c}$$

$$\left[n^{(f)}_{i-\sigma} \, f_{i\sigma}, \mathcal{H}\right] = U_f \, n^{(f)}_{i-\sigma} \, f_{i\sigma} + \Sigma_\ell \, T^{(f)}_{i\ell} \Big\{ n^{(f)}_{i-\sigma} \, f_{\ell\sigma} + f^{+}_{i-\sigma} \, f_{\ell-\sigma} \, f_{i\sigma} -$$

$$- f^{+}_{\ell-\sigma} \, f_{i-\sigma} \, f_{i\sigma} \Big\} + V_{fd} \Big\{ n^{(f)}_{i-\sigma} \, d_{i\sigma} + f^{+}_{i-\sigma} \, d_{i-\sigma} \, f_{i\sigma} - d^{+}_{i-\sigma} \, f_{i-\sigma} \, f_{i\sigma} \Big\} \tag{4-d}$$

These equations are perfectly symmetric for f and d electrons and describe kinetic, Coulomb and mixing effects. Now we follow Roth's approach and calculate the energy and normalization matrices defined respectively by

$$\hat{E}_{ij} = \left\langle \left[\left[A_i, \mathcal{H} \right] , A^{+}_{j} \right]_{+} \right\rangle \tag{5-a}$$

and

$$\hat{N}_{ij} = \left\langle \left[A_i, A^{+}_{j} \right]_{+} \right\rangle \tag{5-b}$$

where the A_i's are members of the set (3).

Using equations (4) and the definition (5-a) one gets for the energy matrix:

$$\hat{E}_{ij} = \left[\begin{array}{cc|cc} T^{(d)}_{ij} + U_d \langle n^d_{-\sigma} \rangle \delta_{ij} & (T^{(d)}_{ij} + U_d \delta_{ij}) \langle n^d_{-\sigma} \rangle & V_{df} \, \delta_{ij} & V_{df} \langle n^f_{-\sigma} \rangle \delta_{ij} \\ (T^{(d)}_{ij} + U_d \delta_{ij}) \langle n^d_{-\sigma} \rangle & U_d \langle n^d_{-\sigma} \rangle \delta_{ij} + \tilde{\Lambda}^{(d)}_{ij\sigma} & V_{df} \langle n^d_{-\sigma} \rangle \delta_{ij} & V_{df} \langle n^d_{-\sigma} \rangle \langle n^f_{-\sigma} \rangle \delta_{ij} \\ \hline V_{fd} \, \delta_{ij} & V_{fd} \langle n^d_{-\sigma} \rangle \delta_{ij} & T^{(f)}_{ij} + U_f \langle n^f_{-\sigma} \rangle \delta_{ij} & (T^{(f)}_{ij} + U_f \delta_{ij}) \langle n^f_{-\sigma} \rangle \\ V_{fd} \langle n^f_{-\sigma} \rangle \delta_{ij} & V_{fd} \langle n^d_{-\sigma} \rangle \langle n^f_{-\sigma} \rangle \delta_{ij} & (T^{(f)}_{ij} + U_f \delta_{ij}) \langle n^f_{-\sigma} \rangle & U_f \langle n^f_{-\sigma} \rangle \delta_{ij} + \tilde{\Lambda}^{(f)}_{ij\sigma} \end{array} \right] \tag{6-a}$$

In the energy matrix (6-a) the dotted lines emphasize the pure d and f contributions (except for mixing contributions in the band shifts $\tilde{\Lambda}$). Translation invariance is used to write $<n_{i-\sigma}> = <n_{-\sigma}>$, and the band shifts $\tilde{\Lambda}^{(d)}_{ij\sigma}$ and $\tilde{\Lambda}^{(f)}_{ij\sigma}$ are defined as:

$$\tilde{\Lambda}^{(d)}_{ij\sigma} = \Lambda^{(d)}_{ij\sigma} - \delta_{ij} V_{df} \left[<f^{+}_{i-\sigma} d_{i-\sigma}> - 2 <n^{(d)}_{i\sigma} f^{+}_{i-\sigma} d_{i-\sigma}>\right]$$

$$\Lambda^{(d)}_{ij\sigma} = T^{(d)}_{ij} <n^{(d)}_{i-\sigma} n^{(d)}_{j-\sigma}> + T^{(d)}_{ij} \left\{<d^{+}_{i-\sigma} d^{+}_{j\sigma} d_{j-\sigma} d_{i\sigma}> - <d^{+}_{j\sigma} d^{+}_{j-\sigma} d_{i-\sigma} d_{i\sigma}>\right\}$$

$$- \delta_{ij} \Sigma_m T^{(d)}_{im} \left\{<d^{+}_{m-\sigma} d_{i-\sigma}> - 2 <n^{(d)}_{i\sigma} d^{+}_{m-\sigma} d_{i-\sigma}>\right\}$$

and a perfectly similar results for $\tilde{\Lambda}^{(f)}_{ij\sigma}$, obtained by replacing d by f and f by d. The off-diagonal elements of (6-a) produce mixing effects among correlated d and f electrons: the results of (6-a) are exact except for the terms $<\left[\left[n^{(d)}_{i-\sigma} d_{i\sigma}, \mathcal{H}\right], n^{(f)}_{j-\sigma} f^{+}_{j\sigma}\right]_{+}>$ and the correspondent to interchange f with d (which are equal); these terms read:

$$<\left[\left[n^{(d)}_{i-\sigma} d_{i\sigma}, \mathcal{H}\right], n^{(f)}_{j-\sigma} f^{+}_{j\sigma}\right]_{+}> = V_{df} <n^{(d)}_{i-\sigma} n^{(f)}_{i-\sigma}> \delta_{ij} -$$

$$V_{df} <d^{+}_{i-\sigma} f_{i-\sigma} f^{+}_{i\sigma} d_{i\sigma}> \delta_{ij} - V_{df} <f^{+}_{i-\sigma} d_{i-\sigma} f^{+}_{i\sigma} d_{i\sigma}> \delta_{ij}$$

We have approximated these expressions using the fact that since d and f bands are not Coulomb interacting, to a first approximation we write:

$$V_{df} <n^{(d)}_{i-\sigma} n^{(f)}_{i-\sigma}> \cong V_{df} <n^{(d)}_{-\sigma}> <n^{(f)}_{-\sigma}> \delta_{ij}$$

and the remaining terms are of third order in the mixing V_{df} if one decouples σ and $-\sigma$ operators. Within this approximation one obtains the terms

$V_{df}\, \langle n^d_{-\sigma}\rangle\langle n^f_{-\sigma}\rangle$ of matrix (6-a). In appendix I we discuss how to deal with these terms correctly and what is their effect.

Now using definition (5-b), and straightforward calculation one gets the normalization matrix and its inverse N^{-1} as:

$$\hat{N} = \left[\begin{array}{cc|cc} \delta_{ij} & \langle n^d_{-\sigma}\rangle\,\delta_{ij} & 0 & 0 \\ \langle n^d_{-\sigma}\rangle\,\delta_{ij} & \langle n^d_{-\sigma}\rangle\delta_{ij} & 0 & 0 \\ \hline 0 & 0 & \delta_{ij} & \langle n^f_{-\sigma}\rangle\,\delta_{ij} \\ 0 & 0 & \langle n^f_{-\sigma}\rangle\delta_{ij} & \langle n^f_{-\sigma}\rangle\,\delta_{ij} \end{array}\right]$$

and

$$\hat{N}^{-1} = \left[\begin{array}{cc|cc} \dfrac{\delta_{ij}}{1-\langle n^d_{-\sigma}\rangle} & -\dfrac{\delta_{ij}}{1-\langle n^d_{-\sigma}\rangle} & 0 & 0 \\ -\dfrac{\delta_{ij}}{1-\langle n^d_{-\sigma}\rangle} & \dfrac{\delta_{ij}}{\langle n^d_{-\sigma}\rangle(1-\langle n^d_{-\sigma}\rangle)} & 0 & 0 \\ \hline 0 & 0 & \dfrac{\delta_{ij}}{1-\langle n^f_{-\sigma}\rangle} & -\dfrac{\delta_{ij}}{1-\langle n^f_{-\sigma}\rangle} \\ 0 & 0 & -\dfrac{\delta_{ij}}{1-\langle n^f_{-\sigma}\rangle} & \dfrac{\delta_{ij}}{\langle n^f_{-\sigma}\rangle(1-\langle n^f_{-\sigma}\rangle)} \end{array}\right] \qquad (7\text{-b})$$

Again dotted lines emphasize the pure d and pure f contributions to the normalization matrix.

It is to be noted that the d-d and the f-f blocks in $\bar{N}$ and $\bar{N}^{-1}$ are identical to Roth's results. Now associated to the basis set (3) we introduce the Green's function matrix $\bar{G}(\omega)$ defined by:

$$\bar{G}_{ij} = \langle\langle A_i , A_j^{+} \rangle\rangle_{\omega} \qquad (8\text{-a})$$

the A_i being the members of (3). Introducing the notation $n_1 = n_{i-\sigma}^{(d)} d_{i\sigma}$ and $n_2 = n_{i-\sigma}^{(f)} f_{i\sigma}$ one gets:

$$\bar{G}_{ij} = \begin{pmatrix} G_{ij}^{dd}(\omega) & G_{ij}^{dn_1}(\omega) & G_{ij}^{df}(\omega) & G_{ij}^{dn_2}(\omega) \\ G_{ij}^{n_1 d}(\omega) & G_{ij}^{n_1 n_1}(\omega) & G_{ij}^{n_1 f}(\omega) & G_{ij}^{n_1 n_2}(\omega) \\ G_{ij}^{fd}(\omega) & G_{ij}^{fn_1}(\omega) & G_{ij}^{ff}(\omega) & G_{ij}^{fn_2}(\omega) \\ G_{ij}^{n_2 d}(\omega) & G_{ij}^{n_2 n_1}(\omega) & G_{ij}^{n_2 f}(\omega) & G_{ij}^{n_2 n_2}(\omega) \end{pmatrix}$$

Now according to Roth's results the matrix $G(\omega)$ satisfies the following equation of motion:

$$(\omega\bar{I} - \bar{E}\cdot\bar{N}^{-1})\cdot\bar{G}(\omega) = \frac{1}{2\pi}\bar{N} \qquad (9)$$

where $\bar{I}$ is the identity matrix. Then next step is to evaluate explicitly the matrix product $\bar{E}\cdot\bar{N}^{-1}$ in order to get the equations of motion for the

Green's function matrix; straightforward matrix multiplication gives (using (6-a) and (7-b)):

$$
\hat{E}\cdot\hat{N}^{-1} = \left[\begin{array}{cc|cc}
T_{ij}^{(d)} & U_d\ \delta_{ij} & V_{df}\ \delta_{ij} & 0 \\
\dfrac{T_{ij}^{(d)}\langle n_{-\sigma}^{d}\rangle-\tilde{\Lambda}_{ij\sigma}^{(d)}}{1-\langle n_{-\sigma}^{d}\rangle} & U_d\delta_{ij}+\dfrac{\tilde{\Lambda}_{ij\sigma}^{(d)}-\langle n_{-\sigma}^{d}\rangle^{2}T_{ij}^{(d)}}{\langle n_{-\sigma}^{d}\rangle(1-\langle n_{-\sigma}^{d}\rangle)} & V_{df}\ \langle n_{-\sigma}^{d}\rangle\delta_{ij} & 0 \\
\hline
V_{fd}\ \delta_{ij} & 0 & T_{ij}^{(f)} & U_f\ \delta_{ij} \\
V_{fd}\langle n_{-\sigma}^{f}\rangle\ \delta_{ij} & 0 & \dfrac{T_{ij}^{(f)}\langle n_{-\sigma}^{f}\rangle-\tilde{\Lambda}_{ij\sigma}^{(f)}}{1-\langle n_{-\sigma}^{f}\rangle} & U_f\delta_{ij}+\dfrac{\tilde{\Lambda}_{ij\sigma}^{(f)}-\langle n_{-\sigma}^{f}\rangle^{2}T_{ij}^{(f)}}{\langle n_{-\sigma}^{f}\rangle(1-\langle n_{-\sigma}^{f}\rangle)}
\end{array}\right]
\qquad (10)
$$

Using the results of (10) one obtains from (9) the coupled equations of motion for the propagators involved in matrix (8-b).

III. DETERMINATION OF THE $G_{ij}^{dd}(\omega)$ PROPAGATOR AND COMPARISON TO HUBBARD APPROXIMATION

Using (9) one gets the following equations of motion:

$$
\omega\ G_{ij}^{dd}(\omega) = \frac{1}{2\pi}\ \delta_{ij} + \Sigma_{\ell}\ T_{i\ell}^{(d)}\ G_{\ell j}^{dd}(\omega) + U_d\ G_{ij}^{n_1 d}(\omega) + V_{df}\ \ G_{ij}^{fd}(\omega) \qquad (11\text{-a})
$$

$$\omega\, G^{n_1 d}_{ij}(\omega) = \frac{1}{2\pi} <n^{d}_{-\sigma}>\delta_{ij} + \Sigma_{\ell} \frac{T^{(d)}_{i\ell}<n^{d}_{-\sigma}> - \tilde{\Lambda}^{(d)}_{i\ell\sigma}}{1 - <n^{d}_{-\sigma}>} G^{dd}_{\ell j}(\omega) + \sum_{\ell} \frac{\tilde{\Lambda}^{(d)}_{i\ell\sigma} - <n^{d}_{-\sigma}>^{2} T^{(d)}_{i\ell}}{<n^{d}_{-\sigma}>(1 - <n^{d}_{-\sigma}>)} G^{n_1 d}_{\ell j}(\omega)$$

$$+ U_d\, G^{n_1 d}_{ij}(\omega) + <n^{d}_{-\sigma}> V_{df}\, G^{fd}_{ij}(\omega) \qquad (11\text{-b})$$

$$\omega\, G^{fd}_{ij}(\omega) = \Sigma_{\ell}\, T^{(f)}_{i\ell}\, G^{fd}_{\ell j}(\omega) + U_f\, G^{n_2 d}_{ij}(\omega) + V_{fd}\, G^{dd}_{ij}(\omega) \qquad (11\text{-c})$$

$$\omega\, G^{n_2 d}_{ij}(\omega) = U_f\, G^{n_2 d}_{ij}(\omega) + \Sigma_{\ell} \frac{\tilde{\Lambda}^{(f)}_{i\ell\sigma} - T^{(f)}_{i\ell}<n^{f}_{-\sigma}>^{2}}{<n^{f}_{-\sigma}>(1 - <n^{f}_{-\sigma}>)} G^{n_2 d}_{\ell j}(\omega) + \Sigma_{\ell} \frac{T^{(f)}_{i\ell}<n^{f}_{-\sigma}> - \tilde{\Lambda}^{(f)}_{i\ell\sigma}}{1 - <n^{f}_{-\sigma}>} G^{fd}_{\ell j}(\omega)$$

$$+ V_{fd} <n^{f}_{-\sigma}>\, G^{dd}_{ij}(\omega) \qquad (11\text{-d})$$

Firstly we want to emphasize that equations (11-a) and (11-c) are exact equations of motion as can be easily verified using equations (4) and the general equation of motion for Green's functions. The approximations of the method are contained in equations (11-b) and (11-d).

Another point we want to stress is that equations (11-a) (11-b) and (11-c) form "separate" blocks in the sense that from (11-a) and (11-b) one gets the propagator $G^{dd}_{ij}(\omega)$ in terms of $G^{fd}_{ij}(\omega)$ which in turn is completely determined by equations (11-c) and (11-d) in terms of $G^{dd}_{ij}(\omega)$.

Then, the effects of d-d correlations are contained in (11-a,b) and the corresponding (f-f) correlations appear in (11-c,d). These f-f correlations are introduced in the problem of d propagation since, through V_{df} mixing d electrons are admixed into the f band and then propagate in presence of f correlations, after what are re-admixed into the d-band. This is the physical origin of the above "separated" blocks. The approximations involved in (11-b) due to the choice of the set (3) are now compared to the standard methods (Hubbard [6]). To do that, the band shift (6-b) is now rewritten in a more convenient way:

$$\tilde{\Lambda}^{(d)}_{ij\sigma} = T^{(d)}_{ij}<n^{d}_{-\sigma}>^2+T^{(d)}_{ij}\left\{<n^{(d)}_{i-\sigma}\;n^{(d)}_{j-\sigma}>-<n^{(d)}_{-\sigma}>^2\right\}+T^{(d)}_{ij}\left\{<d^{+}_{i-\sigma}\;d^{+}_{j\sigma}\;d_{j-\sigma}\;d_{i\sigma}> -\right.$$

$$\left.-<d^{+}_{j\sigma}\;d^{+}_{j-\sigma}\;d_{i-\sigma}\;d_{i\sigma}>\right\} - \delta_{ij}\;\Sigma_m\;T^{(d)}_{im}\left\{<d^{+}_{m-\sigma}\;d_{i-\sigma}>-\;2<n^{(d)}_{i\sigma}\;\;d^{+}_{m-\sigma}\;d_{i-\sigma}>\right\}$$

$$-\;\delta_{ij}\;V_{df}\left\{<f^{+}_{i-\sigma}\;d_{i-\sigma}>-\;2<n^{(d)}_{i\sigma}\;f^{+}_{i-\sigma}\;d_{i-\sigma}>\right\} \qquad (12)$$

The second and third terms of (12) can be rewritten in a quite suggestive way:

$$T^{(d)}_{ij}\left\{<n^{(d)}_{i-\sigma}\;\;n^{(d)}_{j-\sigma}>\;-\;<n^{d}_{-\sigma}>^2\right\} = T^{(d)}_{ij}\;<\left[n^{(d)}_{i-\sigma}\;-\;<n^{(d)}_{-\sigma}>\right]\left[n^{(d)}_{j-\sigma}\;-\;<n^{(d)}_{-\sigma}>\right]> \qquad (13\text{-a})$$

$$T^{(d)}_{ij}\left\{<d^{+}_{i-\sigma}d^{+}_{j\sigma}d_{j-\sigma}d_{i\sigma}>\;-\;<d^{+}_{j\sigma}\;d^{+}_{j-\sigma}\;d_{i-\sigma}\;d_{i\sigma}>\right\} = -T^{(d)}_{ij}<\left[d^{+}_{i-\sigma}d_{j-\sigma}+d^{+}_{j-\sigma}d_{i-\sigma}\right]d^{+}_{j\sigma}d_{i\sigma}> \qquad (13\text{-b})$$

Equations (13-a) and (13-b) describe respectively the total correlation between fluctuations in occupation numbers of $-\sigma$ electrons at sites i and j and the correlated motion of opposite spin electrons between sites i and j.

Equation (11-b) can be rewritten in a clearer way if we introduce the following definitions (suggested by (12) and (13))

$$\alpha_i^\sigma = \frac{1}{<n_{-\sigma}^d>(1-<n_{-\sigma}^d>)}\left\{ \sum_m T_{im}^{(d)}\left[<d_{m-\sigma}^+ \; d_{i-\sigma}> - 2 <n_{i\sigma}^{(d)} \; d_{m-\sigma}^+ \; d_{i-\sigma}>\right]\right.$$

$$\left. + V_{df}\left[<f_{i-\sigma}^+ \; d_{i-\sigma}> - 2 <n_{i\sigma}^{(d)} \; f_{i-\sigma}^+ \; d_{i-\sigma}>\right]\right\} \qquad (14\text{-a})$$

$$\tilde{T}_{ij}^{(d)} = \frac{T_{ij}^{(d)}}{<n_{-\sigma}^d>(1-<n_{-\sigma}^d>)}\left\{<\left[n_{i-\sigma}^{(d)} - <n_{-\sigma}^d>\right]\left[n_{j-\sigma}^{(d)} - <n_{-\sigma}^d>\right]>\right.$$

$$\left. - <\left[d_{i-\sigma}^+ \; d_{j-\sigma} + d_{j-\sigma}^+ \; d_{i-\sigma}\right] d_{j\sigma}^+ \; d_{i\sigma}>\right\} \qquad (14\text{-b})$$

Substituting (12) and (13) in (11-b) and taking into account the definitions (14) one gets the following equation

$$\omega \, G_{ij}^{n_1 d}(\omega) = \frac{1}{2\pi}<n_{-\sigma}^d>\delta_{ij} + <n_{-\sigma}^d> \sum_\ell T_{i\ell}^{(d)} \, G_{\ell j}^{dd}(\omega) + U_d \, G_{ij}^{n_1 d}(\omega) + V_{df}<n_{-\sigma}^d>G_{ij}^{fd}(\omega)$$

$$+ \alpha_i^\sigma\left\{G_{ij}^{n_1 d}(\omega)-<n_{-\sigma}^d>G_{ij}^{dd}(\omega)\right\} + \sum_\ell \tilde{T}_{i\ell}^{(d)}\left\{G_{\ell j}^{n_1 d}(\omega)-<n_{-\sigma}^d>G_{\ell j}^{dd}(\omega)\right\} \qquad (15)$$

In connection with equation (15) we define the following "fluctuation Green's functions"

$$<<\left[n_{i-\sigma}^{(d)} - <n_{-\sigma}^{(d)}>\right]d_{i\sigma}; \; d_{j\sigma}^+>>_\omega = G_{ij}^{n_1 d}(\omega) - <n_{-\sigma}^{(d)}> \; G_{ij}^{dd}(\omega)$$

These functions describe the propagation of a σ- electron from site j to site i in presence of a fluctuation in the occupation number of $-\sigma$ electrons at the site i. The final equation of motion is then:

$$\omega\, G_{ij}^{n_1 d}(\omega) = \frac{1}{2\pi} <n_{-\sigma}^{(d)}> \delta_{ij} + U_d\, G_{ij}^{n_1 d}(\omega) + <n_{-\sigma}^{(d)}> \sum_\ell T_{i\ell}^{(d)}\, G_{\ell j}^{dd}(\omega) + V_{df} <n_{-\sigma}^{(d)}> G_{ij}^{fd}(\omega)$$

$$+ \alpha_i^\sigma << \left[n_{i-\sigma}^{(d)} - <n_{-\sigma}^{d}> \right] d_{i\sigma};\, d_{j\sigma}^{+} >>_\omega + \sum_\ell \tilde{T}_{i\ell}^{(d)} << \left[n_{\ell-\sigma}^{(d)} - <n_{-\sigma}^{d}> \right] d_{\ell\sigma};\, d_{j\sigma}^{+} >>_\omega \qquad (16)$$

The physical interpretation of (16) is more easily seen if one remembers Hubbard approximation [6] to the equations of motion for the Green's function $G_{j}^{n_1 d}(\omega)$. From equation (4-b) and using Hubbard's decoupling one gets [6]

$$\omega\, G_{ij}^{n_1 d}(\omega) = \frac{1}{2\pi} <n_{-\sigma}^{(d)}> \delta_{ij} + U_d\, G_{ij}^{n_1 d}(\omega) + <n_{-\sigma}^{(d)}> \sum_\ell T_{i\ell}^{(d)}\, G_{\ell j}^{dd}(\omega) + V_{df} <n_{-\sigma}^{(d)}> G_{ij}^{fd}(\omega) \qquad (17)$$

Comparison between equations (17) and (16) shows that two extra terms are introduced by the linearization procedure (note that f-d mixing effects are equally treated in both cases); these terms are:

$$\alpha_i^\sigma << \left[n_{i-\sigma}^{d} - <n_{-\sigma}^{d}> \right] d_{i\sigma};\, d_{j\sigma}^{+} >>_\omega \qquad (18\text{-a})$$

$$\sum_\ell \tilde{T}_{i\ell}^{(d)} << \left[n_{\ell-\sigma}^{(d)} - <n_{-\sigma}^{d}> \right] d_{\ell\sigma};\, d_{j\sigma}^{+} >>_\omega \qquad (18\text{-b})$$

and are clearly associated to fluctuations in the occupation numbers of $-\sigma$ spins; in Hubbard's work these fluctuations are completely absent. The first term (18-a) describes one of the effects of $-\sigma$ electron motion; according to definition (14-a) the fluctuation $n_{i-\sigma}^{(d)} - <n_{-\sigma}^{(d)}>$ is connected to two effects: firstly due to the hopping term $T_{im}^{(d)}$, a $-\sigma$ electron may jump from site i to site m during the propagation of a σ electron from j to i. Secondly due to d-f mixing, the $-\sigma$ electron may be admixed into the f band, contributing then to the occupation number fluctuation. The second term (18-b) describes another type of contribution due to $-\sigma$ electron motion which has the form of a "kinetic energy" term. The involved fluctuation propagators still emphasize intra-atomic correlations but at intermediate sites ℓ. These intermediate sites ℓ are connected to the final site i by an effective hopping amplitude $\tilde{T}_{i\ell}^{(d)}$ which takes into account correlated motions. From definition (14-b) one sees that $\tilde{T}_{ij}^{(d)}$ subtracts from the total $-\sigma$ spin correlation function $<\left[n_{i-\sigma}^{(d)} - <n_{-\sigma}^{d}>\right]\left[n_{j-\sigma}^{(d)} - <n_{-\sigma}^{(d)}>\right]>$ the contribution associated to the correlated motion $<\left[d_{i-\sigma}^{+}d_{j-\sigma}+d_{j-\sigma}^{+}d_{i-\sigma}\right]d_{j\sigma}^{+}d_{i\sigma}>$.

Then $\tilde{T}_{ij}^{(d)}$ contains only fluctuation correlations not involving simultaneous transfer of σ and $-\sigma$ electrons from i to j and in this sense is a kinetic like term.

The same type of discussion can be done for equations (11-c) and (11-d) describing f electron correlations; in particular an equation quite similar to (16) can be obtained for the $G_{ij}^{n_2 d}(\omega)$ propagator, just by interchanging d operators by f operators, the physical interpretation being the same.

Whence one has got some insight in the nature of the approximations involved in the choice (3), we proceed discussing the solution of equations (11). We start Fourier transforming equations (11); if one redefines the Fourier transformed band shifts $\Lambda_{k\sigma}$ as:

$$\tilde{\Lambda}_{k\sigma}^{(d)} = <n_{-\sigma}^{d}> (1 - <n_{-\sigma}^{d}>)\, \tilde{W}_{k\sigma}^{(d)} + \varepsilon_k^{(d)} <n_{-\sigma}^{(d)}>^2$$

$$\tilde{\Lambda}_{k\sigma}^{(f)} = <n_{-\sigma}^{f}>(1 - <n_{-\sigma}^{f}>)\, \tilde{W}_{k\sigma}^{(f)} + \varepsilon_k^{(f)} <n_{-\sigma}^{f}>^2 \tag{19}$$

one gets for the Fourier transformed equations (11):

$$(\omega - \varepsilon_k^{(d)})\, G_{k\sigma}^{dd}(\omega) = \frac{1}{2\pi} + U_d\, G_k^{n_1 d}(\omega) + V_{df}\, G_{k\sigma}^{fd}(\omega) \tag{20-a}$$

$$(\omega-U_d)G_{k\sigma}^{n_1 d}(\omega)=\frac{1}{2\pi}<n_{-\sigma}^d>+<n_{-\sigma}^d>(\varepsilon_k^{(d)}-\tilde{W}_{k\sigma}^{(d)})G_{k\sigma}^{dd}(\omega)+\tilde{W}_{k\sigma}^{(d)}G_{k\sigma}^{n_1 d}(\omega)+<n_{-\sigma}^d>V_{df}G_{k\sigma}^{fd}(\omega) \quad (20\text{-b})$$

$$(\omega-\varepsilon_k^{(f)})G_{k\sigma}^{fd}(\omega) = U_f\, G_{k\sigma}^{n_2 d}(\omega) + V_{fd}\, G_{k\sigma}^{dd}(\omega) \quad (20\text{-c})$$

$$(\omega-U_f)G_{k\sigma}^{n_2 d}(\omega)=\tilde{W}_{k\sigma}^{(f)}G_{k\sigma}^{n_2 d}(\omega)+<n_{-\sigma}^f>(\varepsilon_k^{(f)}-\tilde{W}_{k\sigma}^{(f)})G_{k\sigma}^{fd}(\omega)+<n_{-\sigma}^f>V_{fd}\,G_{k\sigma}^{dd}(\omega) \quad (20\text{-d})$$

Now from equations (20-a) and (20-b) one gets for $G_{k\sigma}^{dd}(\omega)$

$$(\omega-\varepsilon_k^{(d)})G_{k\sigma}^{dd}(\omega)=\frac{1}{2\pi}\left\{1+\frac{U_d<n_{-\sigma}^d>}{\omega-U_d-\tilde{W}_{k\sigma}^{(d)}}\right\}+\frac{U_d<n_{-\sigma}^{(d)}>(\varepsilon_k^{(d)}-\tilde{W}_{k\sigma}^{(d)})}{\omega-U_d-\tilde{W}_{k\sigma}^{(d)}}G_{k\sigma}^{dd}(\omega)$$

$$+\frac{U_d<n_{-\sigma}^{(d)}>V_{df}}{\omega-U_d-\tilde{W}_{k\sigma}^{(d)}}G_{k\sigma}^{fd}(\omega)+V_{df}\,G_{k\sigma}^{fd}(\omega) \quad (21)$$

In order to simplify things we only consider here the limit of very strong Coulomb repulsion ($U_d \to \infty$ and $U_f \to \infty$). In these conditions one gets for (21)

$$\left\{\omega-\varepsilon_k^{(d)}(1-<n_{-\sigma}^d>)-<n_{-\sigma}^{(d)}>\tilde{W}_{k\sigma}^{(d)}\right\}G_{k\sigma}^{dd}(\omega)=\frac{1}{2\pi}\left\{1-<n_{-\sigma}^{(d)}>\right\}+V_{df}(1-<n_{-\sigma}^{(d)}>)G_{k\sigma}^{fd}(\omega) \quad (22)$$

Quite similarly from equations (20-c) and (20-d) one obtains for $G_{k\sigma}^{fd}(\omega)$ in this limit:

$$G_{k\sigma}^{fd}(\omega) = V_{fd}\frac{1-<n_{-\sigma}^f>}{\omega-\varepsilon_k^{(f)}(1-<n_{-\sigma}^f>)-<n_{-\sigma}^f>\tilde{W}_{k\sigma}^{(f)}}G_{k\sigma}^{dd}(\omega) \quad (23)$$

One recognizes in equation (23) the Roth propagator for f electrons, $g_{k\sigma}^{ff}(\omega)$, as given by

$$g_{k\sigma}^{ff}(\omega) = \frac{1-<n_{-\sigma}^f>}{\omega-\varepsilon_k^{(f)}(1-<n_{-\sigma}^f>)-<n_{-\sigma}^f>\tilde{W}_{k\sigma}^{(f)}} \quad (24)$$

so equation (22) reads:

$$G_{k\sigma}^{dd}(\omega) = \frac{1}{2\pi} \frac{1 - \langle n_{-\sigma}^{d} \rangle}{\omega - \varepsilon_k^{(d)}(1 - \langle n_{-\sigma}^{d} \rangle) - \langle n_{-\sigma}^{d} \rangle \tilde{W}_{k\sigma}^{(d)} - |V_{df}|^2 (1 - \langle n_{-\sigma}^{(d)} \rangle)\, g_{k\sigma}^{ff}(\omega)} \qquad (25)$$

Equation (25) can now be rewritten in a clearer way if we introduce the f-d renormalized d energies as:

$$\tilde{\varepsilon}_k^{(d)} = \varepsilon_k^{(d)} + |V_{df}|^2\, g_{k\sigma}^{ff}(\omega) \qquad (26\text{-a})$$

$$G_{k\sigma}^{dd}(\omega) = \frac{1}{2\pi} \frac{1 - \langle n_{-\sigma}^{(d)} \rangle}{\omega - \tilde{\varepsilon}_k^{(d)}(1 - \langle n_{-\sigma}^{(d)} \rangle) - \langle n_{-\sigma}^{(d)} \rangle\, \tilde{W}_{k\sigma}^{(d)}} \qquad (26\text{-b})$$

One sees that $G_{k\sigma}^{dd}(\omega)$ is just the pure d electron propagator as obtained by Roth, but now d-electron energies are d-f renormalized as shown in (26-a). A quite similar expression is obtained for the $G_{k\sigma}^{ff}(\omega)$ propagator.

namely:

$$G_{k\sigma}^{ff}(\omega) = \frac{1}{2\pi} \frac{1 - \langle n_{-\sigma}^{(f)} \rangle}{\omega - \tilde{\varepsilon}_k^{(f)}(1 - \langle n_{-\sigma}^{(f)} \rangle) - \langle n_{-\sigma}^{(f)} \rangle\, \tilde{W}_{k\sigma}^{(f)}} \qquad (26\text{-c})$$

There results show that in this picture of actinide metals, the d and f electrons are described by Roth propagators, as in the pure d and pure f cases, except for the mixing effects contained in the renormalized energies $\tilde{\varepsilon}_k^{(d)}$ and $\tilde{\varepsilon}_k^{(f)}$. These results generalize the previous ones [4, 5] for transition metals in the sense that now both the hybridizing bands are correlated bands. The conditions for magnetism follow the same lines as in Roth's, except for the extra difficulty imposed by the presence of hybridization. In appendix III we show, using a method by Kishore and Joshi [7], that analitical expressions for the d and f density of states can be obtained in the approximation of averaged band shifts. Using these density of states the self-consistency program may be performed and the regions of ferromagnetic instability can be determined. Finally, in appendix I one removes the approximations and in computing the energy (6-a). The effect of exactly treating the energy matrix elements is just to introduce effective hybridization matrix elements $|V_{df}^{eff}|^2$ defined by

$$|V_{df}^{eff}|^2 = |V_{df}|^2 (1 + \alpha_\sigma)^2 \tag{26-d}$$

where α_σ is defined by

$$\alpha_\sigma = \frac{\langle \Delta n_{-\sigma}^{(d)} \; \Delta n_{-\sigma}^{(f)} \rangle - \langle | f_{i-\sigma}^{+} \, d_{i-\sigma} + d_{i-\sigma}^{+} \, f_{i-\sigma} | f_{i-\sigma}^{+} \, d_{i\sigma} \rangle}{(1 - \langle n_{-\sigma}^{(d)} \rangle)(1 - \langle n_{-\sigma}^{(f)} \rangle)} \tag{26-e}$$

the expressions (26-b) and (26-c) for d and f propagator remain the same in the exact case, except for the renormalized energies (26-a) which now involve the effective mixing defined above. Equations (26) together with appendix II for the self-consistent determination of α_σ solve completely the problem of the intra-orbital repulsion.

IV. EFFECT OF INTER-ORBITAL REPULSION: FORMULATION AND DISCUSSION OF THE $G^{dd}_{k\sigma}$ PROPAGATOR.

In this part we consider the following model hamiltonian:

$$H = \sum_{i,j,\sigma} T^{(d)}_{ij}\, d^{+}_{i\sigma}\, d_{j\sigma} + \sum_{i,j,\sigma} T^{(f)}_{ij}\, f^{+}_{i\sigma}\, f_{j\sigma} + \sum_{i,\sigma} \left\{ V_{df}\, d^{+}_{i\sigma}\, f_{i\sigma} + \right.$$

$$\left. + V_{fd}\, f^{+}_{i\sigma}\, d_{i\sigma} \right\} + U_{df} \sum_{i} \left\{ n^{(d)}_{i\uparrow}\, n^{(f)}_{i\downarrow} + n^{(d)}_{i\downarrow}\, n^{(f)}_{i\uparrow} \right\} \tag{27}$$

in order to discuss the separate effect of the inter-orbital correlations induced by Coulomb correlation V_{df}. The question now is how to chose the basis set; to do that we firstly write down the equation of motion for the $d_{i\sigma}$ and $f_{i\sigma}$ propagators; one gets:

$$\left[d_{i\sigma}, H \right]_{-} = \sum_{\ell} T^{(d)}_{i\ell}\, d_{\ell\sigma} + U_{df}\, n^{(f)}_{i-\sigma}\, d_{i\sigma} + V_{df}\, f_{i\sigma} \tag{28}$$

$$\left[f_{i\sigma}, H \right]_{-} = \sum_{\ell} T^{(f)}_{i\ell}\, f_{\ell\sigma} + U_{df}\, n^{(d)}_{i-\sigma}\, f_{i\sigma} + V_{fd}\, d_{i\sigma} \tag{29-a}$$

From equations (28) one sees that the equation of motion of $d_{i\sigma}$ and $f_{i\sigma}$ generate respectively the operators $n^{(f)}_{i-\sigma}\, d_{i\sigma}$ and $n^{(d)}_{i-\sigma}\, f_{i\sigma}$. We chose then the following basis set.

$$\left\{ d_{i\sigma};\ n^{(f)}_{i-\sigma}\, d_{i\sigma};\ f_{i\sigma};\ n^{(d)}_{i-\sigma}\, f_{i\sigma} \right\} \tag{29-b}$$

The new operators satisfy the following equations of motion:

$$\left[n^{(f)}_{i-\sigma}\, d_{i\sigma}, H \right]_{-} = U_{df}\, n^{(f)}_{i-\sigma}\, d_{i\sigma} + \sum T^{(d)}_{i\ell}\, n^{(f)}_{i-\sigma}\, d_{\ell\sigma} + \sum_{\ell} T^{(f)}_{i\ell} \left\{ f^{+}_{i-\sigma}\, f_{\ell-\sigma}\, d_{i\sigma} - \right.$$

$$\left. - f^{+}_{\ell-\sigma}\, f_{i-\sigma}\, d_{i\sigma} \right\} + V_{df}\, n^{(f)}_{i-\sigma}\, f_{i\sigma} + V_{fd} \left\{ f^{+}_{i-\sigma}\, d_{i-\sigma}\, d_{i\sigma} - d^{+}_{i-\sigma}\, f_{i-\sigma}\, d_{i\sigma} \right\} \tag{30}$$

and

$$\left[n^{(d)}_{i-\sigma}\, f_{i\sigma},\, H\right] = U_{df}\, n^{(d)}_{i-\sigma}\, f_{i\sigma} + \sum_{\ell} T^{(f)}_{i\ell}\, n^{(d)}_{i-\sigma}\, f_{\ell\sigma} + \sum_{\ell} T^{(d)}_{i\ell} \left\{ d^{+}_{i-\sigma}\, d_{\ell-\sigma}\, f_{i\sigma} - \right.$$

$$\left. - d^{+}_{\ell-\sigma}\, d_{i-\sigma}\, f_{i\sigma} \right\} + V_{fd}\, n^{(d)}_{i-\sigma}\, d_{i\sigma} + V_{df} \left\{ d^{+}_{i-\sigma}\, f_{i-\sigma}\, f_{i\sigma} - f^{+}_{i-\sigma}\, d_{i-\sigma}\, f_{i\sigma} \right\} \quad (31\text{-a})$$

Now using definition (5-a) we calculate the energy matrix $\hat{E}$ as

$$\left[\begin{array}{cc|cc}
T^{(d)}_{ij} + U_{df}\langle n^{(f)}_{-\sigma}\rangle \delta_{ij} & \langle n^{(f)}_{-\sigma}\rangle (T^{(d)}_{ij} + U_{df}\delta_{ij}) & V_{fd}\,\delta_{ij} & V_{fd}\,\langle n^{(d)}_{-\sigma}\rangle\,\delta_{ij} \\
\langle n^{(f)}_{-\sigma}\rangle (T^{(d)}_{ij} + U_{df}\,\delta_{ij}) & U_{df}\langle n^{(f)}_{-\sigma}\rangle \delta_{ij} + \tilde{\Lambda}^{fd}_{ij\sigma} & V_{fd}\langle n^{(f)}_{-\sigma}\rangle \delta_{ij} & V_{fd}\,\Delta_{i\sigma}\,\delta_{ij} \\
\hline
V_{df}\,\delta_{ij} & V_{df}\,\langle n^{(f)}_{-\sigma}\rangle\,\delta_{ij} & T^{(f)}_{ij} + U_{df}\langle n^{(d)}_{-\sigma}\rangle \delta_{ij} & \langle n^{d}_{-\sigma}\rangle (T^{(f)}_{ij} + U_{df}\delta_{ij}) \\
V_{df}\,\langle n^{(d)}_{-\sigma}\rangle\,\delta_{ij} & V_{df}\,\Delta_{i\sigma}\,\delta_{ij} & \langle n^{d}_{-\sigma}\rangle (T^{(f)}_{ij} + U_{df}\delta_{ij}) & U_{df}\langle n^{(d)}_{-\sigma}\rangle \delta_{ij} + \tilde{\Lambda}^{df}_{ij\sigma}
\end{array}\right] \quad (31\text{-b})$$

where the band shifts are now defined by:

$$\tilde{\Lambda}^{fd}_{ij\sigma} = T^{(d)}_{ij}\, \langle n^{(f)}_{i-\sigma}\, n^{(f)}_{j-\sigma}\rangle -$$

$$- T^{(f)}_{ij} \left\langle \left\{ f^{+}_{i-\sigma} f_{j-\sigma} + f^{+}_{j-\sigma} f_{i-\sigma} \right\} d^{+}_{j\sigma} d_{i\sigma} \right\rangle - \delta_{ij} \sum_{\ell} T^{(f)}_{i\ell} \left\{ \langle f^{+}_{\ell-\sigma}\, f_{i-\sigma}\rangle - 2\langle n^{(d)}_{i\sigma}\, f^{+}_{i-\sigma} f_{\ell-\sigma}\rangle \right\}$$

$$- \delta_{ij}\, V_{df} \left\{ \langle d^{+}_{i-\sigma}\, f_{i-\sigma}\rangle - 2\, \langle n^{(d)}_{i\sigma}\, d^{+}_{i-\sigma}\, f_{i-\sigma}\rangle \right\}$$

and a similar expression for $\tilde{\Lambda}^{df}_{ij\sigma}$; finally:

$$\Delta_{i\sigma} = \langle n^{(f)}_{i-\sigma}\, n^{(d)}_{i-\sigma}\rangle - \left\langle \left[f^{+}_{i-\sigma}\, d_{i-\sigma} + d^{+}_{i-\sigma}\, f_{i-\sigma} \right] f^{+}_{i\sigma}\, d_{i\sigma} \right\rangle \quad (32\text{-b})$$

A quite similar discussion to the previous case can be made for the physical meaning of the terms involved in the band shift $\tilde{\Lambda}^{fd}_{ij\sigma}$ and the discussion of $\Delta_{i\sigma}$ will be made latter on.

The normalization matrix and its inverse can be calculated from (5-b); it turns out to be:

$$\left[\begin{array}{cc|cc} \delta_{ij} & \langle n^{(f)}_{-\sigma}\rangle\delta_{ij} & 0 & 0 \\ \langle n^{(f)}_{-\sigma}\rangle\delta_{ij} & \langle n^{(f)}_{-\sigma}\rangle\,\delta_{ij} & 0 & 0 \\ \hline 0 & 0 & \delta_{ij} & \langle n^{(d)}_{-\sigma}\rangle\,\delta_{ij} \\ 0 & 0 & \langle n^{(d)}_{-\sigma}\rangle\,\delta_{ij} & \langle n^{(d)}_{-\sigma}\rangle\delta_{ij} \end{array}\right] \tag{33-a}$$

and its inverse reads:

$$\left[\begin{array}{cc|cc} \dfrac{\delta_{ij}}{1-\langle n^{(f)}_{-\sigma}\rangle} & -\dfrac{\delta_{ij}}{1-\langle n^{(f)}_{-\sigma}\rangle} & 0 & 0 \\ -\dfrac{\delta_{ij}}{1-\langle n^{(f)}_{-\sigma}\rangle} & \dfrac{\delta_{ij}}{\langle n^{(f)}_{-\sigma}\rangle(1-\langle n^{(f)}_{-\sigma}\rangle)} & 0 & 0 \\ \hline 0 & 0 & \dfrac{\delta_{ij}}{1-\langle n^{(d)}_{-\sigma}\rangle} & -\dfrac{\delta_{ij}}{1-\langle n^{(d)}_{-\sigma}\rangle} \\ 0 & 0 & -\dfrac{\delta_{ij}}{1-\langle n^{(d)}_{-\sigma}\rangle} & \dfrac{\delta_{ij}}{\langle n^{(d)}_{-\sigma}\rangle(1-\langle n^{(d)}_{-\sigma}\rangle)} \end{array}\right] \tag{33-b}$$

One sees comparing (33-b) with (7-b) that for the case of U_{df} correlations the positions of the matrix are inverted. Now matrix multiplication gives for $\hat{E}\cdot\hat{N}^{-1}$:

$$
\left[\begin{array}{cc|cc}
T^{(d)}_{ij} & U_{df}\,\delta_{ij} & V_{df}\,\delta_{ij} & 0 \\[2ex]
\dfrac{\langle n^{(f)}_{-\sigma}\rangle T^{(d)}_{ij}-\tilde{\Lambda}^{fd}_{ij\sigma}}{1-\langle n^{(f)}_{-\sigma}\rangle} & U_{df}\delta_{ij}+\dfrac{\tilde{\Lambda}^{fd}_{ij\sigma}-\langle n^{(f)}_{-\sigma}\rangle^{2}T^{(d)}_{ij}}{\langle n^{(f)}_{\sigma}\rangle(1-\langle n^{(f)}_{-\sigma}\rangle)} & V_{df}\delta_{ij}\dfrac{\langle n^{(f)}_{-\sigma}\rangle-\Delta_{i\sigma}}{1-\langle n^{(d)}_{-\sigma}\rangle} & V_{df}\delta_{ij}\dfrac{\Delta_{i\sigma}-\langle n^{(d)}_{-\sigma}\rangle\langle n^{(f)}_{-\sigma}\rangle}{\langle n^{(d)}_{-\sigma}\rangle(1-\langle n^{(d)}_{-\sigma}\rangle)} \\[2ex]
\hline
V_{fd}\,\delta_{ij} & 0 & T^{(f)}_{ij} & U_{df}\,\delta_{ij} \\[2ex]
V_{fd}\delta_{ij}\dfrac{\langle n^{(d)}_{-\sigma}\rangle-\Delta_{i\sigma}}{1-\langle n^{(f)}_{-\sigma}\rangle} & V_{fd}\dfrac{\Delta_{i\sigma}-\langle n^{(f)}_{-\sigma}\rangle\langle n^{(d)}_{-\sigma}\rangle}{\langle n^{(f)}_{-\sigma}\rangle(1-\langle n^{(f)}_{-\sigma}\rangle)} & \dfrac{\langle n^{(d)}_{-\sigma}\rangle T^{(f)}_{ij}-\tilde{\Lambda}^{df}_{ij\sigma}}{1-\langle n^{(d)}_{-\sigma}\rangle} & U_{df}\delta_{ij}+\dfrac{\tilde{\Lambda}^{df}_{ij\sigma}-\langle n^{(d)}_{-\sigma}\rangle^{2}T^{(f)}_{ij}}{\langle n^{(d)}_{-\sigma}\rangle(1-\langle n^{(d)}_{-\sigma}\rangle)}
\end{array}\right]
\tag{34}
$$

Next step is to use the equation of motion for the Green's function matrix $G(\omega)$. Introducing the definitions $n_1 = n^{(f)}_{i-\sigma}\, d_{i\sigma}$ and $n_2 = n^{(d)}_{i-\sigma}\, f_{i\sigma}$ one gets the two <u>exact</u> equations:

$$\omega\, G^{dd}_{ij}(\omega) = \frac{1}{2\pi}\,\delta_{ij} + \sum_{\ell} T^{(d)}_{i\ell}\, G^{dd}_{\ell j}(\omega) + U_{df}\, G^{n_1 d}_{ij}(\omega) + V_{df}\, G^{fd}_{ij}(\omega) \tag{35-a}$$

and

$$\omega\, G^{fd}_{ij}(\omega) = \sum_{\ell} T^{(f)}_{i\ell}\, G^{fd}_{\ell j}(\omega) + U_{df}\, G^{n_2 d}_{ij}(\omega) + V_{df}\, G^{dd}_{ij}(\omega) \tag{35-b}$$

The approximate equation for $G_{ij}^{n_1 d}(\omega)$ reads then:

$$\omega\, G_{ij}^{n_1 d}(\omega) = \frac{1}{2\pi} \langle n_{-\sigma}^{f}\rangle \delta_{ij} + U_{df}\, G_{ij}^{n_1 d}(\omega) + \sum_{\ell} \frac{\tilde{\Lambda}_{i\ell\sigma}^{fd} - \langle n_{-\sigma}^{f}\rangle^{2} T_{i\ell}^{(d)}}{\langle n_{-\sigma}^{f}\rangle (1 - n_{-\sigma}^{f}\rangle)} G_{\ell j}^{n_1 d}(\omega)$$

$$+ \sum_{\ell} \frac{\langle n_{-\sigma}^{f}\rangle T_{i\ell}^{(d)} - \tilde{\Lambda}_{i\ell\sigma}^{fd}}{1 - \langle n_{-\sigma}^{f}\rangle} G_{\ell j}^{dd}(\omega) + V_{df} \frac{\langle n_{-\sigma}^{f}\rangle - \Delta_{i\sigma}}{1 - \langle n_{-\sigma}^{d}\rangle} G_{ij}^{fd}(\omega)$$

$$+ V_{df} \frac{\Delta_{i\sigma} - \langle n_{-\sigma}^{f}\rangle \langle n_{-\sigma}^{d}\rangle}{\langle n_{-\sigma}^{d}\rangle (1 - \langle n_{-\sigma}^{d}\rangle)} G_{ij}^{n_2 d}(\omega) \qquad (35\text{-c})$$

Now we transform a little equation (36-c) in order to make easy comparison to Hubbard's [8] approach; quite similarly to the previous case we define the following quantities:

$$\tilde{\Lambda}_{ij\sigma}^{fd} = \langle n_{-\sigma}^{f}\rangle (1 - \langle n_{-\sigma}^{f}\rangle) \tilde{W}_{ij\sigma}^{fd} + \langle n_{-\sigma}^{f}\rangle^{2}\, T_{ij}^{(d)}$$

$$\tilde{\Lambda}_{ij\sigma}^{df} = \langle n_{-\sigma}^{d}\rangle (1 - n_{-\sigma}^{d}\rangle) \tilde{W}_{ij\sigma}^{df} + \langle n_{-\sigma}^{(d)}\rangle^{2}\, T_{ij}^{(f)} \qquad (35\text{-d})$$

and introduce the quantities α_{σ}^{fd} and α_{σ}^{df} defined through:

$$\Delta_{i\sigma} = \langle n_{-\sigma}^{f}\rangle \langle n_{-\sigma}^{d}\rangle + \left\langle \left[n_{i-\sigma}^{(d)} - \langle n_{-\sigma}^{d}\rangle \right] \left[n_{i-\sigma}^{(f)} - \langle n_{-\sigma}^{f}\rangle \right] \right\rangle - \left\langle \left[f_{i-\sigma}^{+} d_{i-\sigma} + d_{i-\sigma}^{+} f_{i-\sigma} \right] f_{i\sigma}^{+} d_{i\sigma} \right\rangle$$

$$\alpha_{\sigma}^{fd} = \frac{\langle \Delta n_{i-\sigma}^{(d)}\, \Delta n_{j-\sigma}^{(f)}\rangle - \left\langle \left[f_{i-\sigma}^{+} d_{i-\sigma} + d_{i-\sigma}^{+} f_{i-\sigma} \right] f_{i\sigma}^{+} d_{i\sigma} \right\rangle}{\langle n_{-\sigma}^{d}\rangle (1 - \langle n_{-\sigma}^{d}\rangle)}$$

$$\alpha_{\sigma}^{df} = \frac{<\Delta n_{i-\sigma}^{(d)} \; \Delta n_{i-\sigma}^{(f)}> - <\left[f_{i-\sigma}^{+} \; d_{i-\sigma} + d_{i-\sigma}^{+} \; f_{i-\sigma}\right] f_{i\sigma}^{+} \; d_{i\sigma}>}{<n_{-\sigma}^{f}> \; (1-<n_{-\sigma}^{f}>)} \qquad (35\text{-e})$$

One sees from (35-e) that the α's subtracts from the total fluctuation correlation between $-\sigma$ occupation numbers at the d and f bands, the simultaneous mixing of f into d of σ and $-\sigma$ electrons.

Using these definitions one gets:

$$\omega \; G_{ij}^{n_1 d}(\omega) = \frac{1}{2\pi} <n_{-\sigma}^{f}>\delta_{ij} + U_{df} \; G_{ij}^{n_1 d}(\omega) + <n_{-\sigma}^{f}> \sum_{\ell} T_{i\ell}^{(d)} \; G_{\ell j}^{dd}(\omega) + V_{df} \; <n_{-\sigma}^{f}> G_{ij}^{fd}(\omega)$$

$$+ \sum_{\ell} \tilde{W}_{i\ell\sigma}^{fd} G_{\ell j}^{n_1 d}(\omega) - <n_{-\sigma}^{f}> \sum_{\ell} \tilde{W}_{i\ell}^{fd} \; G_{\ell j}^{dd}(\omega)$$

$$+ V_{df} \; \alpha_{\sigma}^{fd} << (n_{i-\sigma}^{(d)} - <n_{-\sigma}^{d}>) f_{i\sigma}; \; d_{j\sigma}^{+}>>_{\omega} \qquad (36)$$

From equation (36) one sees that the first four terms in the right band side are Hubbard's approximation for the equation of motion of $G_{ij}^{n_1 d}(\omega)$ propagator. The terms involving the band shift can be written as $\sum_{\ell} \tilde{W}_{i\ell\sigma}^{fd} << (n_{i-\sigma}^{(f)} - <n_{-\sigma}^{f}>) \; d_{i\sigma}; \; d_{j\sigma}^{+}>>_{\omega}$ and correspond as discussed previously to the effect of electron fluctuations associated to propagation within the d-band. Finally last term describes fluctuation effects associated to the mixing V_{df}. A quite similar equation can be written for the propagator $G_{ij}^{n_2 d}(\omega)$.

Now we solve by Fourier transformation the above equations; one gets:

$$(\omega-\varepsilon_k^{(d)})\ G_{k\sigma}^{dd}(\omega) = \frac{1}{2\pi} + U_{df}\ G_k^{n_1 d}(\omega) + V_{df}\ G_{k\sigma}^{fd}(\omega) \qquad (37\text{-a})$$

$$(\omega-U_{df})G_{k\sigma}^{n_1 d}(\omega) = \frac{1}{2\pi}<n_{-\sigma}^f> + \tilde{W}_k^{fd}\ G_{k\sigma}^{n_1 d}(\omega) + <n_{-\sigma}^{(f)}>(\varepsilon_k^{(d)}-\tilde{W}_{k\sigma}^{fd})G_{k\sigma}^{dd}(\omega)$$

$$+ V_{df}<n_{-\sigma}^f>G_{k\sigma}^{fd}(\omega) + V_{df}\ \alpha_\sigma^{fd}\ G_{k\sigma}^{n_2 d}(\omega) - V_{df}\ \alpha^{fd}<n_{-\sigma}^d>G_{k\sigma}^{fd} \qquad (37\text{-b})$$

$$(\omega-\varepsilon_k^{(f)})\ G_{k\sigma}^{fd}(\omega) = U_{df}\ G_{k\sigma}^{n_2 d}(\omega) + V_{fd}\ G_{k\sigma}^{dd}(\omega) \qquad (37\text{-c})$$

$$(\omega-U_{df})G_{k\sigma}^{n_2 d}(\omega) = \tilde{W}_{k\sigma}^{df}\ G_{k\sigma}^{n_2 d}(\omega) + <n_{-\sigma}^d>(\varepsilon_k^{(f)}-\tilde{W}_{k\sigma}^{df})G_{k\sigma}^{fd}(\omega) + V_{fd}<n_{-\sigma}^d>G_{k\sigma}^{dd}(\omega)$$

$$+ V_{fd}\ \alpha^{df}\ G_{k\sigma}^{n_1 d} - V_{fd}\ \alpha^{df}<n_{-\sigma}^f>G_{k\sigma}^{dd}(\omega) \qquad (37\text{-d})$$

Equations (38) are then solved in the limit of very strong inter-orbital repulsion ($U_{df} \to \infty$); one gets for $G_{k\sigma}^{fd}(\omega)$:

$$G_{k\sigma}^{fd}(\omega) = V_{fd}\ \frac{1 - <n_{-\sigma}^d> + \alpha^{df}<n_{-\sigma}^f>}{\omega - \varepsilon_k^{(f)}(1-<n_{-\sigma}^d>)-<n_{-\sigma}^d>\tilde{W}_{k\sigma}^{df}}\ G_{k\sigma}^{dd}(\omega) \qquad (38)$$

Comparison to equation (24) shows that one gets a propagator quite similar to g_{ff} propagator except for the fact that now due to d-f correlations the narrowing factor is $(1 - <n_{-\sigma}^d>)$ instead of $(1- <n_{-\sigma}^f>)$ which would appear if we had intra f band correlations.

For the $G_{k\sigma}^{dd}(\omega)$ propagator one gets:

$$\left\{\omega-\varepsilon_k^{(d)}(1-<n_{-\sigma}^f>)-<n_{-\sigma}^f>\tilde{W}_{k\sigma}^{fd} - |V_{df}|^2\ \frac{(1-<n_{-\sigma}^f>-\alpha^{fd}<n_{-\sigma}^d>)(1-<n_{-\sigma}^d>+\alpha^{df}<n_{-\sigma}^f>)}{\omega - \varepsilon_k^{(f)}(1-<n_{-\sigma}^d>)-<n_{-\sigma}^{(d)}>W_{k\sigma}^{df}}\right\}G_{k\sigma}^{dd}(\omega)$$

$$= \frac{1}{2\pi}(1 - <n_{-\sigma}^f>) \qquad (39)$$

Expression (39) can be modified to give a much more simple interpretation; we start rewriting the coefficients

$$1 - \langle n^f_{-\sigma}\rangle + \alpha^{fd}\langle n^d_{-\sigma}\rangle = (1 - \langle n^f_{-\sigma}\rangle)(1 + \alpha_\sigma)$$

$$1 - \langle n^d_{-\sigma}\rangle + \alpha^{df}\langle n^f_{-\sigma}\rangle = (1 - \langle n^d_{-\sigma}\rangle)(1 + \alpha_\sigma) \qquad (40\text{-a})$$

where the quantity α_σ is defined as:

$$\alpha_\sigma = \frac{\langle \Delta n^d_{i-\sigma}\, \Delta n^f_{i-\sigma}\rangle - \langle \left[f^+_{i-\sigma}\, d_{i-\sigma} + d^+_{i-\sigma}\, f_{i-\sigma}\right] f^+_{i\sigma}\, d_{i\sigma}\rangle}{(1 - \langle n^d_{-\sigma}\rangle)(1 - \langle n^f_{-\sigma}\rangle)} \qquad (40\text{-b})$$

Expression (40-a) suggests the definition of an effective V_{df} mixing through

$$\left|V^{eff}_{df\sigma}\right|^2 = |V_{df}|^2(1 + \alpha_\sigma)^2 \qquad (40\text{-c})$$

and the definition of the pure f propagator

$$g^{ff}_{k\sigma}(\omega) = \frac{1 - \langle n^d_{-\sigma}\rangle}{\omega - \varepsilon^{(f)}_k(1 - \langle n^d_{-\sigma}\rangle) - \langle n^d_{-\sigma}\rangle\, \tilde{W}^{df}_{k\sigma}} \qquad (40\text{-d})$$

the final expression for the d propagator is then:

$$G^{dd}_{k\sigma}(\omega) = \frac{1}{2\pi}\; \frac{1 - \langle n^f_{-\sigma}\rangle}{\omega - \tilde{\varepsilon}^{(d)}_k(1 - \langle n^f_{-\sigma}\rangle) - \langle n^f_{-\sigma}\rangle\, W^{fd}_{k\sigma}} \qquad (41\text{-a})$$

where the V_{df} renormalized d electron energy reads:

$$\tilde{\varepsilon}^{(d)}_k = \varepsilon^{(d)}_k + \left|V^{eff}_{df}\right|^2 g^{ff}_{k\sigma}(\omega) \qquad (41\text{-b})$$

CONCLUSIONS

In paragraphs II and III the one-electron propagators are obtained for the case of intra-orbital and inter-orbital repulsion. In both cases one obtains Roth-like propagators, with V_{df} renormalized one electron f or d energies. These results generalize the previous ones obtained for transition metal systems [4, 5], in the sense that the hybridizing bands are now Coulomb correlated bands. In the case of inter-orbital correlations, the exact energy matrix is taken into account, and the consequence of taking it exact is to introduce an effective mixing matrix element $|V_{df}^{eff}|^2$, which accounts for the effect of fluctuations in occupation numbers of d and f bands. In appendix I we show that for the case of intra-orbital repulsion we can remove the approximations introduced in discussing the energy matrix. One recovers essentially the same result as in the inter-orbital case, obtaining for the effective mixing the same formal expression for the correction α_σ defined in (40-b). In appendix II we use the method of Roth to show that the self-consistent determination of the correlation functions involved in the definition of α_σ is feasible. Finally the method of Kishore and Joshi [7] is used to derive analytical expressions for the density of states (cf. appendix III). The program of performing the self-consistent determination of the occupation numbers (and consequently the magnetic state) can be performed in the same lines as in Roth's paper, except for the hybridization effects which are treated in the same way as Kishore and Joshi, using the density of states of appendix III.

APPENDIX I

In this appendix we remove the approximation introduced in part II, for the energy matrix $\hat{E}$. The matrix elements are identical to those defined in (6-a) except for the elements $<\left[\left[n^{(d)}_{i-\sigma}\ d_{i\sigma}, \mathcal{H}\right], n^{(f)}_{j-\sigma}\ f^{+}_{j\sigma}\right]_{+}>$ and $<\left[\left[n^{(f)}_{i-\sigma}\ f_{i\sigma}, \mathcal{H}\right], n^{(d)}_{j-\sigma}\ d^{+}_{j\sigma}\right]_{+}>$. These matrix elements (which are equal) now have the exact value of:

$$<\left[\left[n^{(d)}_{i-\sigma}\ d_{i\sigma}, \mathcal{H}\right], n^{(f)}_{j-\sigma}\ f^{+}_{j\sigma}\right]_{+}> = V_{df}\ \delta_{ij}\left\{ <n^{(d)}_{i-\sigma}\ \ n^{(f)}_{i-\sigma}> - \right.$$

$$\left. - <\left[d^{+}_{i-\sigma}f_{i-\sigma} + f^{+}_{i-\sigma}\ d_{i-\sigma}\right]\ f^{+}_{i\sigma}\ d_{i\sigma}> \right\} = V_{df}\ \delta_{ij}\ \Delta_{i\sigma} \qquad \text{(A1-1)}$$

Again we separate the fluctuation terms as:

$$\Delta_{i\sigma} = <n^{d}_{-\sigma}><n^{(f)}_{-\sigma}> + <\Delta n^{(d)}_{i-\sigma}\ \Delta n^{(f)}_{i-\sigma}> - <\left[d^{+}_{i-\sigma}\ f_{i-\sigma} + f^{+}_{i-\sigma}\ d_{i-\sigma}\right]\ f^{+}_{i\sigma}\ d_{i\sigma}> \qquad \text{(A1-2)}$$

We see that the first term is the approximation used in part II, which correspond then to neglect the fluctuation terms defined in (A1-2). The matrix $\hat{E}\cdot\hat{N}^{-1}$ reads now:

$$\left[\begin{array}{cc:cc}
T^{(d)}_{ij} & U_d\ \delta_{ij} & V_{df}\ \delta_{ij} & 0 \\
\dfrac{T^{(d)}_{ij}<n^{d}_{-\sigma}>-\tilde{\Lambda}^{(d)}_{ij\sigma}}{1-<n^{d}_{-\sigma}>} & U_d\delta_{ij}+\dfrac{\tilde{\Lambda}^{(d)}_{ij\sigma}-<n^{d}_{-\sigma}>^{2}T^{(d)}_{ij}}{<n^{d}_{-\sigma}>(1-<n^{d}_{-\sigma}>)} & V_{df}\delta_{ij}\dfrac{<n^{d}_{-\sigma}>-\Delta_{i\sigma}}{1-<n^{f}_{-\sigma}>} & V_{df}\delta_{ij}\dfrac{\Delta_{i\sigma}-<n^{d}_{-\sigma}><n^{f}_{-\sigma}>}{<n^{f}_{-\sigma}>(1-<n^{f}_{-\sigma}>)} \\
\hdashline
V_{fd}\ \delta_{ij} & 0 & T^{(f)}_{ij} & U_f\ \delta_{ij} \\
V_{fd}\dfrac{<n^{f}_{-\sigma}>-\Delta_{i\sigma}}{1-<n^{d}_{-\sigma}>} & V_{df}\delta_{ij}\dfrac{\Delta_{i\sigma}-<n^{d}_{-\sigma}><n^{f}_{-\sigma}>}{<n^{d}_{-\sigma}>(1-<n^{d}_{-\sigma}>)} & \dfrac{T^{(f)}_{ij}<n^{f}_{-\sigma}>-\tilde{\Lambda}^{(f)}_{ij\sigma}}{1-<n^{(f)}_{-\sigma}>} & U_f\delta_{ij}+\dfrac{\tilde{\Lambda}^{(f)}_{ij\sigma}-<n^{f}_{-\sigma}>^{2}T^{(f)}_{ij}}{<n^{f}_{-\sigma}>(1-<n^{f}_{-\sigma}>)}
\end{array}\right] \qquad \text{(A1-3)}$$

Comparison to (10) shows that if one neglects in (A1-3) the fluctuation terms envolved in $\Delta_{i\sigma}$ one recovers the results of part II. Introducing the definitions

$$\tilde{\Lambda}^{(d)}_{ij\sigma} = \langle n^d_{-\sigma}\rangle (1-\langle n^d_{-\sigma}\rangle)\, \tilde{W}^{(d)}_{ij\sigma} + T^{(d)}_{ij} \langle n^d_{-\sigma}\rangle^2$$

$$\tilde{\Lambda}^{(f)}_{ij} = \langle n^f_{-\sigma}\rangle(1-\langle n^f_{-\sigma}\rangle)\, \tilde{W}^{(f)}_{ij\sigma} + T^{(f)}_{ij} \langle n^f_{-\sigma}\rangle^2$$

$$\alpha^d_\sigma = \frac{\langle \Delta n^{(d)}_{i-\sigma}\, \Delta n^{(f)}_{i-\sigma}\rangle - \langle |f^+_{i-\sigma}\, d_{i-\sigma} + d^+_{i-\sigma}\, f_{i-\sigma}| f^+_{i\sigma}\, d_{i\sigma}\rangle}{\langle n^f_{-\sigma}\rangle\, (1-\langle n^f_{-\sigma}\rangle)}$$

and a similar definition for α^f_σ, one obtains the equations of motion for the propagators as an example, the equation of motion for d-propagator are:

$$\omega\, G^{dd}_{ij}(\omega) = \frac{1}{2\pi}\, \delta_{ij} + \sum_\ell T^{(d)}_{i\ell}\, G^{dd}_{\ell j}(\omega) + U_d\, G^{n_1 d}_{ij}(\omega) + V_{df}\, G^{fd}_{ij}(\omega) \qquad \text{(A1-4)}$$

$$\begin{aligned}(\omega-U)G^{n_1 d}_{ij}(\omega) = {} & \frac{1}{2\pi}\, \delta_{ij} \langle n^d_{-\sigma}\rangle + \langle n^d_{-\sigma}\rangle \sum_\ell T^{(d)}_{i\ell}\, G^{dd}_{\ell j}(\omega) + V_{df} \langle n^d_{-\sigma}\rangle\, G^{fd}_{ij}(\omega) \\ & + \sum_\ell \tilde{\tilde{W}}^{(d)}_{i\ell} \langle\langle \left[n^{(d)}_{\ell-\sigma} - \langle n^d_{-\sigma}\rangle\right] d_{\ell\sigma};\, d^+_{j\sigma}\rangle\rangle_\omega \\ & + V_{df}\, \alpha^d_\sigma \langle\langle \left[n^{(f)}_{i-\sigma} - \langle n^f_{-\sigma}\rangle\right] f_{i\sigma};\, d^+_{j\sigma}\rangle\rangle_\omega \end{aligned} \qquad \text{(A1-5)}$$

Quite similar equations are obtained for the G^{fd}_{ij} and $G^{n_2 d}_{ij}$ propagators. Now we see from equation (A1-5) that the first three terms are just Hubbard approximations for the equation of motion of $G^{n_1 d}_{ij}$. The fourth term include fluctuations of d occupation numbers as discussed in part II.

Finally last term describe f band fluctuations induced by the mixing V_{df}, and this is the new term associated to $\Delta_{i\sigma} \neq <n^f_{-\sigma}> <n^d_{-\sigma}>$. Now solution of these equations by Fourier transformation give the following result:

$$G^{dd}_{k\sigma}(\omega) = \frac{1}{2\pi} \frac{1 - <n^d_{-\sigma}>}{\omega - \tilde{\varepsilon}^{(d)}_k (1 - <n^d_{-\sigma}>) - <n^{(d)}_{-\sigma}> \tilde{W}^{(d)}_{k\sigma}} \tag{A1-6}$$

where the renormalized d-band energy is

$$\tilde{\varepsilon}^{(d)}_k = \varepsilon^{(d)}_k + \left| V^{eff}_{df} \right|^2 g^{ff}_{k\sigma} \tag{A1-7}$$

the effective matrix element being defined as

$$\left| V^{eff}_{df} \right|^2 = |V_{df}|^2 (1 + \alpha_\sigma)$$

$$\alpha_\sigma = \frac{<\Delta n^d_{-\sigma} \, \Delta n^f_{-\sigma}> - <\left[f^+_{i-\sigma} d_{i-\sigma} + d^+_{i-\sigma} f_{i-\sigma} \right] f^+_{i\sigma} d_{i\sigma}>}{(1 - <n^d_{-\sigma}>)(1 - <n^f_{-\sigma}>)} \tag{A1-8}$$

and $g^{ff}_{k\sigma}$ is defined in equation (24).

One sees that α_σ is <u>formally</u> identical to the corresponding of the inter-orbital case, but its value is certainly different (cf. Appendix II).

APPENDIX II

In this appendix we describe the procedure to be used in the determina tion of the correlation functions involved in the definition of α_σ, equation (40-b) there correlation functions are $<n^{(d)}_{i-\sigma} \; n^{(f)}_{i-\sigma}>$, $<f^+_{i-\sigma} d_{i-\sigma} f^+_{i\sigma} d_{i\sigma}>$ and $<d^+_{i-\sigma} \; f_{i-\sigma} \; f^+_{i\sigma} \; d_{i\sigma}>$. We are interested in the limit $U_d \to \infty$ and $U_f \to \infty$, corresponding to the first case, namely intra-orbital repulsion. In this limit the correlation function $<f^+_{i-\sigma} \; d_{i-\sigma} \; f^+_{i\sigma} \; d_{i\sigma}>$ vanishes so one needs to determine only the two remaining functions we use the general equation of motion for Roth's method:

$$\omega <<A_n, B>>_\omega = \frac{1}{2\pi} <\left[A_n, B\right]_+> + \sum_m K_{nm} <<A_m, B>>_\omega \qquad \text{(A2-1)}$$

where the matrix K is equal to $E \cdot N^{-1}$, and the operator B is arbitrary. Now we chose appropriate operators B in order to get the correlation functions. One has

$$< d^+_{j\sigma} \; d_{i\sigma} \; n^{(f)}_{j\sigma}> = F_\omega <<d_{i\sigma}, n^{(f)}_{j\sigma} \; d^+_{j\sigma}>>_\omega \; , \quad B = n^{(f)}_{j\sigma} \; d^+_{j\sigma} \qquad \text{(A2-2)}$$

From (A2-2), taking i=j one obtains $<n^{(d)}_{i\sigma} \; n^{(f)}_{j\sigma}>$. For the basis set (3) one gets the following anticommutators:

$$<\left[d_{i\sigma}, n^{(f)}_{j\sigma} \; d^+_{j\sigma}\right]_+> = <n^{(f)}_{i\sigma}> \delta_{ij}$$

$$<\left[f_{i\sigma}, n^{(f)}_{j\sigma} \; d^+_{j\sigma}\right]_+> = - <d^+_{i\sigma} \; f_{i\sigma}> \delta_{ij} \qquad \text{(A2-3)}$$

$$<\left[n^{(d)}_{i-\sigma} \; d_{i\sigma}, n^{(f)}_{j\sigma} \; d^+_{j\sigma}\right]_+> = <n^{(d)}_{i-\sigma} \; n^{(f)}_{j\sigma}> \delta_{ij}$$

$$<\left[n^{(f)}_{i-\sigma} \; f_{i\sigma}, n^{(f)}_{j\sigma} \; d^+_{j\sigma}\right]_+> = -<n^{(f)}_{i\sigma} \; d^+_{i\sigma} \; f_{i\sigma}> \delta_{ij} \to 0 \quad \text{as } U_f \to \infty$$

Substituting the results (A2-3) in equation (A2-1) and using $\hat{E}\cdot\hat{N}^{-1}$ given in (10) we obtain a set of equations for the propagators $<<A_n, B>>_\omega$. When solved this system gives $<<d_{i\sigma}, B>>_\omega$ expressed in terms of the correlation functions (A2-3). However this procedure introduces a new function namely $<n_{i-\sigma}^{(d)} \; n_{i\sigma}^{(f)}>$ which we now determine. One has:

$$<f_{j\sigma}^{+} \; f_{i\sigma} \; n_{j-\sigma}^{(d)}> = F_\omega <<f_{i\sigma}, n_{j-\sigma}^{(d)} \; f_{j\sigma}^{+}>>_\omega, \quad B = n_{j-\sigma}^{(d)} \; f_{j\sigma}^{+} \tag{A2-4}$$

Taking i=j one gets

$$<n_{i\sigma}^{(f)} \; n_{i-\sigma}^{(d)}> = <n_{i-\sigma}^{(d)} \; n_{i\sigma}^{(f)}>$$

For the new choice of B one has the following anticommutators:

$$\begin{aligned}
&<\left[f_{i\sigma}, n_{j-\sigma}^{(d)} \; f_{j\sigma}^{+}\right]_{+}> = <n_{i-\sigma}^{(d)}> \delta_{ij} \\
&<\left[d_{i\sigma}, n_{j-\sigma}^{(d)} \; f_{j\sigma}^{+}\right]_{+}> = 0 \\
&<\left[n_{i-\sigma}^{(d)} \; d_{i\sigma}, n_{j-\sigma}^{(d)} \; f_{j\sigma}^{+}\right]_{+}> = 0 \\
&<\left[n_{i-\sigma}^{(f)} \; f_{i\sigma}, n_{j-\sigma}^{(d)} \; f_{j\sigma}^{+}\right]_{+}> = <n_{i-\sigma}^{(d)} \; n_{i-\sigma}^{(f)}> \delta_{ij}
\end{aligned} \tag{A2-5}$$

Again the Green's function $<<f_{i\sigma}, B>>_\omega$ can be expressed in terms of the functions (A2-5). Since the new set of equations (A2-5) regenerate the correlation function $<n_{i-\sigma}^{(d)} \; n_{i-\sigma}^{(f)}>$ this enables us to completely determine the function $<n_{i-\sigma}^{(d)} \; n_{i-\sigma}^{(f)}>$.

Finally it remains to calculate the correlation function $<d_{i-\sigma}^{+} \; f_{i-\sigma} \; f_{i\sigma}^{+} \; d_{i\sigma}>$. To do that one takes:

$$< d^{+}_{j-\sigma} f_{j-\sigma} f^{+}_{j\sigma} d_{i\sigma} > = F_{\omega} << d_{i\sigma}, d^{+}_{j-\sigma} f_{j-\sigma} f^{+}_{j\sigma} >>_{\omega}, \quad B = d^{+}_{j-\sigma} f_{j-\sigma} f^{+}_{j\sigma}$$

the anticommutators associated to this new choice are:

$$< \left[d_{i\sigma}, d^{+}_{j-\sigma} f_{j-\sigma} f^{+}_{j\sigma} \right]_{+} > = 0$$

$$< \left[f_{i\sigma}, d^{+}_{j-\sigma} f_{j-\sigma} f^{+}_{j\sigma} \right]_{+} > = < d^{+}_{j-\sigma} f_{j-\sigma} > \delta_{ij}$$

$$< \left[n^{d}_{i-\sigma} d_{i\sigma}, d^{+}_{j-\sigma} f_{j-\sigma} f^{+}_{j\sigma} \right]_{+} > = - < d^{+}_{i-\sigma} f_{i-\sigma} f^{+}_{i\sigma} d_{i\sigma} > \delta_{ij}$$

$$< \left[n^{(f)}_{i-\sigma} f_{i\sigma}, d^{+}_{j-\sigma} f_{j-\sigma} f^{+}_{j\sigma} \right]_{+} > = < n^{(f)}_{i\sigma} d^{+}_{i-\sigma} f_{i-\sigma} > \delta_{ij} \to 0 \quad \text{as} \quad U_f \to \infty$$

Then, one can solve for $<< d_{i\sigma}, B >>_{\omega}$ in terms of known quantities. Using a quite similar procedure one can determine the functions involved in α_{σ} for the case of inter-orbital repulsion using equation (34) for $\hat{E} \cdot \hat{N}^{-1}$.

APPENDIX III

We calculate now the explicit form of the density of states for the intra-orbital case, using the method of Kishore and Joshi [7]. We start from the -d-propagator

$$G^{dd}_{k\sigma}(\omega) = \frac{1}{2\pi} \frac{1 - <n^{d}_{-\sigma}>}{\omega - \varepsilon^{(d)}_{k}(1 - <n^{d}_{-\sigma}>) - <n^{d}_{-\sigma}> \tilde{W}^{(d)}_{\sigma} - \left| V^{eff}_{df} \right|^{2} (1 - <n^{d}_{-\sigma}>) \dfrac{1 - <n^{f}_{-\sigma}>}{\omega - \varepsilon^{(f)}_{k}(1 - <n^{f}_{-\sigma}>) - <n^{f}_{-\sigma}> \tilde{W}^{(f)}_{\sigma}}} \quad \text{(A3-1)}$$

where $\tilde{W}^d_\sigma$ and $\tilde{W}^f_\sigma$ are averaged band shifts (Roth [3]).

We adopt here the model for the band structure consisting of homothetic bands, namely:

$$\varepsilon_k^{(d)} = \varepsilon_k$$
$$\varepsilon_k^{(f)} = A\ \varepsilon_k + A' \qquad \text{(A3-2)}$$

the constant A < 1 reducing the width of the f-band. We introduce also the following definitions:

$$\bar{\varepsilon}_{k\sigma} = \varepsilon_k(1 - \langle n^d_{-\sigma}\rangle) + \langle n^d_{-\sigma}\rangle\ \tilde{W}^d_\sigma$$

and

$$\left|\tilde{V}_{df}\right|^2 = \left|V^{eff}_{df}\right|^2 (1-\langle n^d_{-\sigma}\rangle)(1-\langle n^f_{-\sigma}\rangle) \qquad \text{(A3-3)}$$

Using these definitions equation (A3-1) becomes:

$$G^{dd}_{k\sigma}(\omega) = \frac{1}{2\pi}\ \frac{1 - \langle n^d_{-\sigma}\rangle}{\omega - \bar{\varepsilon}_{k\sigma} - \dfrac{|\tilde{V}_{df}|^2}{\omega - (A\ \varepsilon_k + A')(1-\langle n^f_{-\sigma}\rangle) - \langle n^f_{-\sigma}\rangle\ \tilde{W}^f_\sigma}} \qquad \text{(A3-4)}$$

Now we write the denominator of $g^{ff}_{k\sigma}$ in terms of the $\bar{\varepsilon}_\sigma$ energies

$$\omega - (A\ \varepsilon_k + A')(1 - \langle n^f_{-\sigma}\rangle) - \langle n^f_{-\sigma}\rangle\ \tilde{W}^f_\sigma = \omega - (\bar{A}\ \bar{\varepsilon}_{k\sigma} + \bar{A}'_\sigma) \qquad \text{(A3-5)}$$

where the new "effective mass" $\bar{A}$ is:

$$\bar{A} = A\ \frac{(1 - \langle n^f_{-\sigma}\rangle)}{1 - \langle n^d_{-\sigma}\rangle} \qquad \text{(A3-6)}$$

and

$$\bar{A}'_\sigma = -A \frac{1 - \langle n^f_{-\sigma}\rangle}{1 - \langle n^d_{-\sigma}\rangle} \langle n^d_{-\sigma}\rangle \tilde{W}^d_\sigma + A'(1-\langle n^f_{-\sigma}\rangle) + \langle n^f_{-\sigma}\rangle \tilde{W}^{(f)}_\sigma$$

Using equation (A3-5) we get

$$G^{dd}_{k\sigma}(\omega) = \frac{1}{2\pi} \frac{(1-\langle n^d_{-\sigma}\rangle)\left[\omega-(\bar{A}\,\bar{\varepsilon}_{K\sigma} + \bar{A}'_\sigma)\right]}{(\omega-\bar{\varepsilon}_{k\sigma})\left[\omega-(\bar{A}\,\bar{\varepsilon}_{k\sigma} + \bar{A}'_\sigma)\right] - |\tilde{V}_{df}|^2} \qquad \text{(A3-7)}$$

Or in terms of the poles of the denominator:

$$G^{dd}_{k\sigma}(\omega) = \frac{1}{2\pi} \frac{(1-\langle n^d_{-\sigma}\rangle)\left[\omega-(\bar{A}\,\bar{\varepsilon}_{k\sigma} + \bar{A}_{\sigma'}\right]}{(\omega - \omega^+_k)(\omega-\omega^-_k)} \qquad \text{(A3-8)}$$

the density of d-states is then:

$$n^d(\omega)=\sum_k \left|(1-\langle n^d_{-\sigma}\rangle)(\omega-\bar{A}\,\bar{\varepsilon}_{k\sigma} - \bar{A}'_\sigma)\right| \delta\left[(\omega-\omega^+_k)(\omega-\omega^-_k)\right] \qquad \text{(A3-9)}$$

Now following Kishore and Joshi we define functions $g^+(\omega)$ and $g^-(\omega)$ through the relation:

$$(\omega-\omega^+_k)(\omega-\omega^-_k) = \bar{A}(g^+(\omega) - \bar{\varepsilon}_{k\sigma})(g^-(\omega) - \bar{\varepsilon}_{k\sigma}) \qquad \text{(A3-10)}$$

this equation defines a second order equation for the g's which is

$$\bar{A}\,g^2(\omega) - \left\{(\bar{A}+1)\omega - \bar{A}'_\sigma\right\} g(\omega) + \omega^2 - \bar{A}'_\sigma\,\omega - |\tilde{V}_{df}|^2 = 0 \qquad \text{(A3-11a)}$$

whose solutions are ($p = \pm$):

$$g^p(\omega) = \frac{1}{2\bar{A}} \left\{(\bar{A}+1)\omega - \bar{A}'_\sigma + p\left[((\bar{A}-1)\omega+\bar{A}'_\sigma)^2 + 4\,\bar{A}\,|\tilde{V}_{df}|^2\right]^{\frac{1}{2}}\right\} \qquad \text{(A311b)}$$

Using (A3-10) in (A3-9) one gets:

$$n^d(\varepsilon) = \sum_p \left| \frac{(1-\langle n^d_{-\sigma}\rangle)(\omega-\bar{A}\; g^p(\omega)-\bar{A}'_\sigma)}{\bar{A}\;(g^+(\omega)\; - g^-(\omega))} \right| \sum_k \; \delta\left[g^p(\omega)\; - \bar{\varepsilon}_{k\sigma}\right] \qquad \text{(A3-12)}$$

Now one has:

$$\sum_k \delta\left[g^p(\omega) - \bar{\varepsilon}_{k\sigma}\right] = \sum_k \delta\left\{(1-\langle n^d_{-\sigma}\rangle)\left[\frac{g^p(\omega)\; - \langle n^d_{-\sigma}\rangle\; \tilde{W}^{(d)}_\sigma}{1-\langle n^d_{-\sigma}\rangle} - \varepsilon_k\right]\right\}$$

$$= \frac{1}{|1-\langle n^d_{-\sigma}\rangle|}\; N\left(\frac{g^p(\omega) - \langle n^d_{-\sigma}\rangle\; \tilde{W}^d_\sigma}{1\; -\; \langle n^d_{-\sigma}\rangle}\right)$$

where $N(\omega)$ is the density of states associated to ε_k.

Finally:

$$n^d(\omega) = \sum_p \left| \frac{\omega-\bar{A}g^p(\omega)-\bar{A}'_\sigma}{A(g^+(\omega)\; - g^-(\omega))} \right| \; N \left(\frac{g^p(\omega)\; - \langle n^d_{-\sigma}\rangle\; \tilde{W}^{(d)}_\sigma}{1\; - \langle n^d_{-\sigma}\rangle}\right) \qquad \text{(A3-13)}$$

Quite similarly one derives an expression for the f density of states.

* * *

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