Theory of Strongly Correlated Electron Systems.
III. Including Correlation Effects into Electronic Structure Calculations

U. Lundin\(^1\), I. Sandalov\(^{1,2}\), O. Eriksson\(^1\)

\(^1\)Condensed Matter Theory group, Uppsala University, Box 530, SE-751 21 Uppsala, Sweden
\(^2\)Dept. of Physics, Linköping University, SE-581 83 Linköping, Sweden

(March 21, 2022)

In previous papers\(^1\),\(^2\) we showed that a division of the \(f\)-shell into two subsystems gives a better understanding of cohesive properties as well as the general behavior of lanthanide systems. In this paper we present numerical computations using the suggested method. We show that the picture is consistent with most experimental data, e.g. the equilibrium volume and electronic structure in general. Compared to standard energy band calculations, or to calculations based on the self-interaction correction and LDA+U, in the present approach \(f\)-(non-\(f\))-mixing interaction is decreased by spectral weights of the many-body states of the \(f\)-ion are involved.

I. INTRODUCTION

Strongly correlated electrons show a rich variety of physical properties, e.g. heavy Fermion behavior, partial localization and unconventional superconductivity. Normal \textit{ab initio} electronic structure calculations performed for these systems have proven to be unable to capture the essential features of these systems. The reason for this is mainly that the LDA underestimates the strong correlations caused by the local part of the Coulomb interaction among the electrons. The standard model for the lanthanides corrects for this via imposing a condition on the \(f\)-electrons which is not present in the standard LDA DFT scheme: i) \(f\)-electrons should be treated as atomic like and localized; ii) the \(f\)-shell contains an integral number, \(n\), of electrons. However, it has been argued\(^2\), that already the cohesive properties signal a deviation from the standard model.

In a previous paper\(^2\), we presented an idea how normal band structure calculations could be extended to treat systems with strongly correlated electrons, that is an improvement on normal methods such as LDA+U, SIC or treating the \(f\)-electrons as atomic like. Indeed it was demonstrated that the cohesive properties, such as e.g. equilibrium volume is better described with this method. The calculation\(^2\) has been performed within the linear muffin-tin orbital method within the spherical approximation (LMTO-ASA). The comparison with the results of normal LMTO-ASA calculation has shown that the latter contains two type of errors: one comes from the spherical approximation and another from the underestimated electron correlations. Here we have implemented these many-body corrections in a full-potential all-electron relativistic energy band method, in order to obtain a description as accurate as possible, and we have tested our theory for the light lanthanides. These elements are an excellent testing ground for any theory that tries to incorporate electron correlations, since so much is known experimentally about them. For this reason, we have chosen to test our theory on these materials, before addressing more involved systems such as the heavy Fermion materials, UPt\(_3\) and CeCu\(_2\)Si\(_2\) and possibly the \(\delta\)-phase of Pu.

The paper is organized as follows. In Section II we derive the equations that form the ground for the calculations, in Section III we describe the details of the numerical implementation, and Section IV contains the results. Finally we conclude in Section V.

II. DERIVATION OF THE KOHN-SHAM LIKE EQUATIONS

The main motivations of this work are to derive expressions for corrections from strong electron correlations to standard methods of \textit{ab initio} methods. We also want to make an attempt to understand, from a many-body theory point of view, the mechanism of localization of \(f\)-electrons, that may be described phenomenologically by self-interaction correction (SIC), and the so called LDA+U method. As we shall see the method allows us to capture features of correlated systems such as e.g. the correlation narrowing of bands. The full description of our approach, as well as notations, will be given in ref\(^3\), and we present here only some of the theoretical details, how we have implemented the theory numerically as well as the results of some of our calculations.

We formulate the problem following the ideology presented in ref\(^3\), namely, that the one-to-one correspondence between the ARF (the approximation of renormalized Fermions) series and the one from weak-coupling perturbation
theory allows to use the same analytical form for the exchange-correlation potential. Moreover, our theory includes renormalized mixing, hopping, overlap matrices and charge density, by the spectral weights of the many-electron ion states that we involve. The ARF can be viewed as the Hubbard-I approximation which is extended to the case of full Coulomb interaction. This approximation is the simplest possible, but since it is exact in the atomic limit it is expected to give reasonable results in the case of very strong correlations.

Now let us establish a connection between the secular equations solved in electronic structure calculations (ESC) and Green function methods for strongly correlated electrons. In order to do this we need to define the Hamiltonians for the two problems. First, when solving the Kohn-Sham equation we have to solve a secular equation, which looks like,

$$ (\epsilon \mathcal{O}_{jL,j_1L_1} - h^c_{jL,j_1L_1}) \chi_{j_1L_1} = 0, $$

where $\mathcal{O}_{jL,j_1L_1}$ is the overlap matrix between the cite-centered basis-functions, $\chi_{j_1L_1}$; $j$ is the site index and $L$ is a composite index $L = (l, m_l, \sigma)$. $\epsilon_{jL}$ is the energy for the orbital, and $h^c_{jL,j_1L_1}$ is the Hamiltonian matrix element which will be defined below. Let us first consider the $f$-electrons as localized. We, therefore, write the Hamiltonian for the band structure method with the $f$-electrons separated from the other conduction electrons. Denoting the operators for $f$- and conduction-electrons with $f$ and $c$, respectively, the ESC Hamiltonian is

$$ \mathcal{H} = \sum_{k,L_1,L_2} h^c_{1L_1,L_2}(k) c^{\dagger}_{L_1L_2}c^c_{L_2} + \sum_{j_1\nu_1} \epsilon_{j_1\nu_1} f^{\dagger}_{j_1\nu_1}f_{j_1\nu_1} 
 + \sum_{j_1\nu_1,j_2\nu_2} t^{\dagger}_{j_1j_2\nu_1\nu_2} f^{\dagger}_{j_1\nu_1}f_{j_2\nu_2} 
 + \sum_{k,L_1,j_2\nu_2} V_{j_1L_1,j_2\nu_2}[c^{\dagger}_{L_1L_2}f_{j_2\nu_2} + f^{\dagger}_{j_2\nu_2}c_{L_1L_2}], $$

where the matrix elements come from the expectation value of the Hamiltonian with respect to the basis functions

$$ h^c_{1L_1,L_2}(k) = \langle \chi_{1L_1}(k)|\mathcal{H}|\chi_{2L_2}(k)\rangle. $$

The index $L$ is used solely for conduction electrons. We denote the $f-f$ hopping by $t$ and the mixing between $c$ and $f$ by $V$. Combined indices for the $f$’s are denoted with $\nu$. The operators fulfill the commutation relation

$$ \{a_{j_1L_1}, a^{\dagger}_{j_2L_2}\} = \delta_{j_1L_1,j_2L_2}, $$

where $a$ is either a $c-$ or an $f$-operator. The Hamiltonian, Eq. (3), is a DFT Hamiltonian using either LDA or any other approximation for the exchange-correlation potential, i.e.

$$ \mathcal{H} = \frac{p^2}{2m} + \int d\mathbf{r} d\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + V^{XC}(\rho(\mathbf{r})) + V_{en}, $$

where $V^{XC}(\rho(\mathbf{r}))$ is the exchange correlation potential and $V_{en}$ is the interaction of electrons with nuclei. From these definitions we can define Green functions which we can use to make a comparison to the case for strongly correlated electrons.

Obviously, the same problem can be written in terms of Green functions (GFs). Denoting the Fermionic Green functions $F$ and separating the $c-$ and $f$-electrons we can write the GF, $F$, in super matrix form,

$$ F_{\nu_1L_1,L_2}(k, i\omega) F^{\dagger}_{\nu'_1L_1,L_2}(k, i\omega) F^{\dagger}_{\nu'_2L_2}(k, i\omega) F_{\nu_2L_2}(k, i\omega), $$

$$ \text{def} \frac{1}{i} \left( \langle T c_{j_1\nu_1}^{\dagger} c_{j_2\nu_2} L_2^c \rangle \langle T f_{j_1L_1}^{\dagger} f_{j_2L_2} L_2^f \rangle \right)_{k,\omega}, $$

where $T$ is the chronological ordering operator. Further, we denote the time Fourier transform by a small $\omega$ and $k$-space Fourier transform with a small $k$. Taking into account the commutation relations, Eq. (3) in this representation, we obtain the equation of motion for the Green functions (the $k$ in $\mathcal{O}(k)$ is omitted for convenience):
Thus, if we multiply both sides of Eq.(6) by the overlap matrix, then, the inverse of the GF coincides with the bracket in Eq.(6), and the corresponding secular determinant gives a band structure coinciding with Eq.(1). Let us now move to the problem of strongly correlated electrons. We will work with the multiple-orbital periodical Anderson model (MO-PAM) in terms of Hubbard operators. The latter are defined as projection (transition) operators acting on the many-body states of an ion, \( i \), in the position \( \mathbf{R}_i \), as,

\[
X_i^{\Gamma, \Gamma'} \overset{\text{def}}{=} |i, \Gamma \rangle \langle \Gamma', i |.
\]

(8)

Here \( |\Gamma_n\rangle \) is an \( n \)-particle state constructed out of orbitals from the ESC, \( |\Gamma_n\rangle = f_1 f_2 \ldots f_n |0\rangle \). To simplify the notations we denote the Fermi-like transitions \( [\Gamma, \Gamma'] \) with Roman letters \( a, b, \ldots \). The commutator relation for the \( X \)-operators are written in terms of structure constants \( \epsilon \) of the algebra

\[
\{X^a, X^b\} = \sum_\xi \epsilon_{\xi}^{a, b} Z^\xi,
\]

(9)

where \( Z^\xi \) denotes a Bose-like transition, changing the particle number with an even number. The Fermion \( f \)-operators can be expressed in terms of \( X \)-operators (or vice versa), i.e.,

\[
f_{j\nu} = \sum_{\Gamma, \Gamma'} (\Gamma | f_{j\nu} | \Gamma') X_j^{\Gamma, \Gamma'} = \sum_a (f_{j\nu})^a X_j^a.
\]

(10)

The model for the strongly correlated electrons, the multiple-orbital periodical Anderson model (MO-PAM) (Eq.(2) with hopping \( t=0 \)), is expressed in terms of \( X \)-operators using the relation in Eq.(8),

\[
\mathcal{H} = \sum_{k, L_1} \epsilon_{kL_1} c_{kL_1}^\dagger c_{kL_1} + \sum a E^a_j Z^a_j + \sum_{k, l, j, j' \neq a} \left( (f_{j\nu_2})^a c_{kL_1}^\dagger X_j^a + \text{c.c.} \right),
\]

(11)

where the band-structure for the \( c \) electrons is \( \epsilon_{kL_1} \) and \( E^a_j = \epsilon^a (f_{j\nu_2})^a (f_{j\nu_2})^a \). Within the ARF we are dealing with the same effective Hamiltonian as Eq.(2) with the exception that instead of the term \( \sim \epsilon^0 f_{j\nu} f_{j'\nu'} \) we have to write the term describing the many-electron states of an ion,

\[
\mathcal{H}^a_j = \sum_{j, \Gamma} E_{j, \Gamma} \mathcal{H}^{\Gamma}_j,
\]

(12)

and \( f \)-operators should be rewritten in terms of Hubbard operators (see ref.4). Then the effective Hamiltonian acquires the form of the multi-orbital periodical Anderson model (MO-PAM). The equations for the Green functions for the multiple-orbital periodical Anderson model (MO-PAM) in the Hubbard-I approximation within a non-orthogonal basis set have the following form,

\[
\begin{align*}
&\left[ \delta_{jj_2} \delta_{LL_2} i \partial_t - \mathcal{O}^{-1}_{jL_1, jL_1} h^{\xi}_{ee_{jL_1}} \right] G^{a^\dagger}_{jL_1, jL_1}(t, t') = i \delta(t - t') \langle \{ c_{jL_1}, \eta_j^1 \} \rangle \\
&+ \left[ \mathcal{O}^{-1}_{jL_2, jL_2} (f_{j\nu})^a \mathcal{E}_{\xi}^{\dagger} \right] + \mathcal{O}^{-1}_{jL_1, jL_1} V_{jL_1, jL_2}(f_{j\nu})^a \\
&\times G^{a^\dagger}_{jL_2, jL_2}(t, t') + \mathcal{O}^{-1}_{jL_1, jL_1}(f_{j\nu})^a V^{*}_{jL_1, jL_2}(f_{j\nu})^a \delta_{\xi}^{\langle \xi_j \rangle} G^{a^\dagger}_{jL_2, jL_2}(t, t'),
\end{align*}
\]

(13)

\[
\begin{align*}
&[i \partial_t - \Delta_a] G^{a^\dagger}_{jL_1, jL_1} = i \delta(t - t') \langle \{ X_j^a, \eta_j^1 \} \rangle \\
&+ \left[ \mathcal{O}^{-1}_{jL_1, jL_1} h^{\xi}_{ee_{jL_1}} + \mathcal{O}^{-1}_{jL_1, jL_1} V^{*}_{jL_1, jL_2} \right] \\
&\times (f_{j\nu})^a \delta_{\xi}^{\langle \xi_j \rangle} G^{a^\dagger}_{jL_2, jL_2}(t, t') + \mathcal{O}^{-1}_{jL_1, jL_1} V_{jL_1, jL_2}(f_{j\nu})^a \delta_{\xi}^{\langle \xi_j \rangle} (f_{j\nu})^a G^{a^\dagger}_{jL_2, jL_2}(t, t'),
\end{align*}
\]

(14)
where $\eta$ denotes either a $c$ or a $X$-operator, $\Delta_n$ is the energy of the transition $a$ (e.g. if $a = \Gamma_{n-1}, \Gamma_n$ then $\Delta_n = E_{\Gamma_n} - E_{\Gamma_{n-1}}$). We simplify the model further neglecting the energy differences between different transitions in the lower Hubbard sub-band, i.e., between $n$- and $(n-1)$-electron states. Then all these transitions have the same energy, $\Delta_1$. The same will be assumed about the upper transitions, between $(n+1)$- and $n$-electron states; they then have the energy $\Delta_2$. We assume that the lower transition lies so much lower in energy than the bottom of all conduction bands that the overlap integrals as well as mixing interaction of conduction electrons with these transitions are equal to zero. Therefore, for $\alpha = [\Gamma_{n-1}, \Gamma_n]$, the GFs $G_{j\alpha, j'}^X = 0$ and
\[
G_{j\alpha, j'}^{\alpha} = \delta_{\alpha\alpha'}\delta_{jj'} \frac{P_\alpha}{i\omega - \Delta_\alpha}.
\] (15)

This GF gives the equation for the population numbers
\[
N_{\Gamma_n} = (N_{\Gamma_{n-1}} + N_{\Gamma_n})f(\Delta_\alpha),
\] (16)
where $f(\Delta_\alpha)$ is Fermi function for the transition $\Delta_\alpha$. Since $\beta\Delta_\alpha \gg 1$, $N_{\Gamma_{n-1}} = \exp(-\beta\Delta_\alpha)N_{\Gamma_n}$. The lower population numbers are negligible and only $N_{\Gamma_n}$ and $N_{\Gamma_{n+1}}$ have nonzero values, while Eq (14) becomes an identity. This allows us to formulate the system of equations for GFs which contains only upper transitions. After Fourier transformations $t \rightarrow t' \rightarrow i\omega$ and $R_j \rightarrow R_j' \rightarrow k$, the system of equations acquires the following form:

\[
\frac{\delta_{LL} i\omega - O_{L_L}^{-1}(k)h_{LL}^{-1}(k)}{O_{L_L}^{-1}(k)} \frac{G_{\alpha\eta\eta}^{\eta\eta}(k, i\omega) = i\{\{c_{jL}, \eta_j'\}\}}{\text{k}}
\]
\[
+ [O_{L_L\mu}^{-1}(k)(f_\mu)^a E_{L_L\mu}^{a} \alpha_{\mu} + O_{L_L\mu}^{-1}(k)V_{L_L\mu}(k)(f_\mu)^b]G_{a}^{X\eta}(k, i\omega)
\]
\[
+ O_{L_L\mu}^{-1}(k)(f_\mu)^a V_{LL}^{-1}(k)(f_\mu)^b \delta_{X\eta}(Z\xi)G_{a}^{\eta\eta}(k, i\omega),
\] (17)

\[
[i\omega - \Delta_\alpha]G_{X\eta}^{X\eta}(k, i\omega) = i\delta(t - t')(\{X\eta, \eta_j'\})
\]
\[
+ [O_{L_L\mu}^{-1}(k)h_{LL}^{-1}(k) + O_{L_L\mu}^{-1}(k)V_{L_L\mu}(k)]
\]
\[
\times (f_\mu)^b \delta_{X\eta}(Z\xi)G_{a}^{\eta\eta}(k, i\omega)
\]
\[
+ O_{L_L\mu}^{-1}(k)\frac{V_{L_L\mu}(k)(f_\mu)^b \delta_{X\eta}(Z\xi)}{\phi}\frac{G_{a}^{X\eta}(k, i\omega)}{\text{k}}.
\] (18)

Let us now try to identify if we, from the general equations, can establish some connection to ESC. In ESC calculations $n$ orbitals are localized and (for $f$-systems) $14 - n$ orbitals are delocalized. This picture naturally arises in our approach within the orbital representation, where the wave function is taken in the simple form $[\Gamma_n] = f_{\mu_1}f_{\mu_2}...f_{\mu_n}0) \equiv |0\>$. Since in this case the occupied orbitals are fixed, there are only one such state $|\eta\>$. Then, the states with $(n+1)$ electrons arise when one of the orbitals $\varphi_{\nu_1}, \varphi_{\nu_2}, ..., \varphi_{\nu_{n-1}}$, which are empty in the state $|0\>$, is occupied in the state $|\Gamma_\nu\> = f_{\mu_1}f_{\mu_2}...f_{\mu_n}0)$. Any of the states $|\Gamma_\nu\>$ contains only one $f$-orbital of the type $\nu$ (which is delocalized due to its overlap and mixing with the conduction-electron orbitals), each particular transition $\alpha : [\Gamma_{n+1}] \rightarrow [\Gamma_\nu]$, or, more explicitly, $f_\nu|0\> \rightarrow |0\>$, described by the Hubbard operator $X^\alpha$, this representation can be relabeled by $X^\nu$ since it fills the orbital $\nu$. Thus, one can indeed establish a one-to-one correspondence between filling unoccupied $f$-orbitals and the many-electron transitions. But this is possible only in this particular representation, which ignores the Hund rules and, therefore, ignores an essential part of the problem. Moreover, even in this representation the degeneracy must enter the equations explicitly, since it always exist if we ignore the intra shell spin-spin exchange (first Hund rule) and orbital-orbital exchange (second Hund rule). For the less than half filled shell this is not very essential unless we consider spin excitations and do not take into account the crystal field since the requirement of maximal spin and orbital moment makes the ground-state wave function unique. Let us rewrite our equations in the following matrix form, taking into account the above assumption (here, for a brevity we omit the $k$-dependence in $h(k), V(k)$, and $O(k)$):

\[
\left(\begin{array}{c}
\delta_{LL} i\omega - O_{L_L}^{-1}(k)h_{LL}^{-1}(k) - O_{L_L}^{-1}(f_{\nu_1})V_{LL}^{-1}(f_{\nu_1})aP_a
\end{array}\right)
\]
\[
\left(\begin{array}{c}
O_{L_L}^{-1}(k)h_{LL}^{-1}(k) + O_{L_L}^{-1}(V_{LL}^{-1}(k))(f_\mu)^b
\end{array}\right)
\]
\[
\times \left(\begin{array}{c}
G_{\alpha\eta\eta}^{\eta\eta}(i\omega)
\end{array}\right)
\]
\[
\left(\begin{array}{c}
G_{a\alpha\alpha}^{\alpha\alpha}(i\omega)
\end{array}\right)
\]
\[
= i \left(\begin{array}{c}
O_{L_L}^{-1}(f_{\nu_1})(f_\mu)^a P_a
\end{array}\right)
\]
\[
\left(\begin{array}{c}
O_{L_L}^{-1}(f_{\nu_1})P_a
\end{array}\right).
\] (19)

1 Without coupling to the lattice this state may be degenerate.
The on-site matrix elements \((f_{ij})^\alpha_{\nu_1}\), which in the case of an orthogonal basis set give ”selection rules”, give a non-zero value: 
\[(f_{ij})^\alpha_{\nu_1} = \langle 0 | p_{\nu_1} \cdot f_{ij} | 0 \rangle = O_{\nu_1\nu}^{-1}.
\] For example, for the case of one c-orbital and two delocalized f-orbitals \(O_{\nu_1\nu}^{-1} = [(1 - \delta_{\nu_1\nu}) O_{\nu} \Delta_{\nu_{12}} + \delta_{\nu_1\nu} (O_{\nu} - |\nu\rangle \langle \nu|) / \det \mathcal{O} \), where \(\det \mathcal{O} = \left| \mathcal{O}_{\nu_{1}c} \right| = |\nu_{1}\rangle \langle \nu_{1}|.\)
If we restrict ourselves with the accuracy \(\sim o(O^1)\), i.e. neglect the matrix elements \(\sim |O_{\nu\nu}|^2\), then \(O_{\nu_1\nu}^{-1} \approx \delta_{\nu_1\nu}.\)
If we ignore the multiplet structure, then all energies \(\Delta_a = \Delta_2\) coincide, and we find that the combination of population numbers \(p[I_{\nu_1\nu}; I_{\nu_1\nu+1}] = S[I_{\nu_1\nu}; I_{\nu_1\nu+1}] = \{I_{\nu_1\nu}; I_{\nu_1\nu+1}\} = \{0\} \langle f_{ij} | 0 \rangle \approx 1.\)

Let us now introduce the effective Fermions \(\tilde{F}\) from the Green function \(\tilde{G}\).

Thus, diagonalizing this equation in these approximations we obtain the following system of equations
\[
\begin{align*}
  \left( \begin{array}{cc}
    [\delta_{LL} i\omega - O_{L_{1}L_{2}}^{-1} h_{L_{1}L_{2}} - O_{L_{1}}^{-1} V_{L_{1}L_{2}} P] & [O_{L_{1}L_{2}}^{-1} \Delta_2 + O_{L_{1}L_{2}}^{-1} V_{L_{1}L_{2}}] \\
    [O_{L_{1}L_{2}}^{-1} h_{L_{1}L_{2}} + O_{L_{1}L_{2}}^{-1} V_{L_{1}L_{2}}] & [i\omega - \Delta_a - O_{L_{1}L_{2}}^{-1} V_{L_{1}L_{2}} P]
  \end{array} \right) \\
  \left( \begin{array}{c}
    G_{L_{1}L_{2}}^{-1}(k, i\omega) \\
    G_{L_{1}L_{2}}(k, i\omega)
  \end{array} \right)
\end{align*}
\]
\] (20)

Let us now introduce the effective Fermions \(\tilde{F} \equiv X/\sqrt{P}\) with the help of the following transformation:
\[(L_{\mathbf{w}} - \Omega)G = P \Rightarrow U(L_{\mathbf{w}} - \Omega)U^{-1}g = UPU,
\] (21)
where the block-matrix \(U\) is:
\[
U = \left( \begin{array}{cc}
  1 & 0 \\
  0 & \frac{1}{\sqrt{P}}
\end{array} \right)
\] (22)

and \(g = U^\dagger g U\). After this transformation Eq.(20) acquires the following form:
\[
\begin{align*}
  \left( \begin{array}{cc}
    [\delta_{LL} i\omega - O_{L_{1}L_{2}}^{-1} h_{L_{1}L_{2}} - (O_{L_{1}}^{-1} \sqrt{P})(V_{L_{1}L_{2}} \sqrt{P})] & [(O_{L_{1}}^{-1} \sqrt{P}) \Delta_2 + O_{L_{1}}^{-1} (V_{L_{1}L_{2}} \sqrt{P})] \\
    [(O_{L_{1}}^{-1} \sqrt{P}) h_{L_{1}L_{2}} + O_{L_{1}}^{-1} V_{L_{1}L_{2}}] & [i\omega - \Delta_a - (O_{L_{1}}^{-1} \sqrt{P})(V_{L_{1}L_{2}} \sqrt{P})]
  \end{array} \right) \\
  \left( \begin{array}{c}
    g_{L_{1}L_{2}}^{-1}(k, i\omega) \\
    g_{L_{1}L_{2}}(k, i\omega)
  \end{array} \right)
\end{align*}
\] (23)

Let us compare the system of equations, Eq.(23), for the GFs, \(G\), written in orbital representation, with the system of equations for the Fermion GFs, \(F\), corresponding to the secular problem in normal electronic structure calculations, Eq.(7). We find that the systems coincide if we renormalize mixing and overlap matrices as follows:
\[
O_{L_{1}nu}^{-1} \rightarrow \tilde{O}_{L_{1}nu}^{-1} = O_{L_{1}nu}^{-1} \sqrt{P}, \quad V_{L_{1}nu} \rightarrow \tilde{V}_{L_{1}nu} = V_{L_{1}nu} \sqrt{P},
\] (24)
and put \(O_{L_{1}nu}^{-1} = \delta_{\nu\nu'}\). Thus, the matrix equation for the renormalized GFs, \((L_{\mathbf{w}} - \tilde{\Omega}^{-1} \tilde{V})g = \tilde{\Omega}^{-1}\), can be rewritten in the form containing the standard secular matrix used in the electronic structure calculations
\[
(\tilde{\Omega}_{\mathbf{w}} - \tilde{V})g = \mathbf{I}.
\] (25)

Now, using the standard procedure of Cholesky decomposition, \(\mathbf{I} = (\tilde{\Omega}_{\mathbf{w}} - \tilde{V})g = (Z_{\mathbf{w}} \mathbf{Z} - \tilde{V})g\), we can rewrite this equation in terms of an effective Hamiltonian:
\[
(L_{\mathbf{w}} - Z^{-1} \tilde{V} \mathbf{Z}^{-1}) \mathbf{Z}g \mathbf{Z} = \mathbf{I},
\] (26)
or,
\[
(L_{\mathbf{w}} - h)\tilde{g} = \mathbf{I}.
\] (27)

Thus, diagonalizing this equation in \(k\)-space, we find the renormalized band structure. The parameter \(P\), is calculated from the Green function \(G_{XX}\).

In the paper [13] we have shown that within the ARF each graph contributing to the Green function and the self-energy in the weak coupling perturbation theory has its counter-part in the strong-coupling theory and, therefore, one can use the same expression for the weak coupling GF as in the case of weak coupling theory but with the renormalizations shown in Eq.(24).

2 In general, of course, this is a matrix \(M \times M\), where \(M\) is number of transitions.
III. ELECTRONIC STRUCTURE CALCULATION IN THE ARF

Since the secular equations to be solved include, in an explicit way, many body corrections in ARF, we will refer to this calculation as an electronic structure calculation in ARF (ESC-ARF). Let us now describe the numerical implementation of the ESC-ARF method. Following the analysis of the previous section, as well as our previous work, the f-states are divided into a lower level and an upper level. In ESC the electrons are normally separated into core and valence electrons, and it is not hard, in practice, to include the many body corrections derived in the previous section. The lower transitions are simply single electron core levels in the ESC, and the upper transitions are all described by the set of equations described in the previous section. Due to the analogy made between the obtained equations, Eq. (23) and the standard secular equation solved for the Kohn-Sham equation, Eq. (7), one needs to perform only relatively small modifications to any electronic structure method. Implemented in a full potential, site centered basis function method (to be specific, a linear muffin-tin orbital method) the Hamiltonian matrix has the schematic form as is shown in Fig. 1. The energy of the upper transition, \( \Delta_2 \) may be used as a variable input parameter, but it can also be taken from bremsstrahlung isochromat spectra (BIS). The values obtained in this way are presented in Table I.

| element | Ce | Pr | Nd | Pm* | Sm |
|---------|----|----|----|-----|----|
| f-peak | 3.52 | 2.27 | 1.68 | 1.08^a | 0.64 |

*Pm is radioactive, this value is a fit between Nd and Sm

The renormalizing factor, \( \sqrt{P} \), which should multiply the Hamiltonian and the overlap matrices in the places specified in Fig. 2 has to be calculated self-consistently. Since we only take into account the states, \( \Gamma_n \) and \( \Gamma_{n+1} \), there are only two non-zero population numbers, \( N_{\Gamma_n} \) and \( N_{\Gamma_{n+1}} \), which gives rise to a single \( P \). Further, we disregard the multiplet structure and therefore all transitions have the same energy, \( \Delta_1 \) for the lower level and \( \Delta_2 \) from the upper level. The population numbers distribute as follows;

\[
\begin{align*}
\begin{cases}
n_I = n \cdot N_I + (n + 1) \sum_{\nu} N_{2 \nu} & \text{def} = n + \eta \\
N_I + \sum_{\nu} N_{2 \nu} & \equiv 1,
\end{cases}
\end{align*}
\]

where \( n + 1 \) are the degeneracy of the states \( \Gamma_n \) and \( \Gamma_{n+1} \), respectively, and \( \nu \) is an index of the available single-electron orbitals to construct \( \Gamma_{n+1} \) from \( \Gamma_n \). If we assume that all upper transitions (this number is the same as the number of available single-electron orbitals) are occupied symmetrically, we find that \( \sum_{\nu} N_{2 \nu} = n N_2 \), i.e. \( N_2 = \eta / (14 - n) \) and \( N_1 = 1 - \eta \). Then, the renormalizing factor will be

\[
P = 1 - \frac{14 - (n + 1)}{14 - n} \eta.
\]

The \( f \)-electron locator GF becomes

\[
G_1 = G_2 = \ldots = G_n = \frac{1 - \eta}{i \omega_n - \Delta_1} + \frac{\eta}{i \omega_n - \Delta_2}
\]

and

\[
G_{\nu} = \frac{1}{i \omega_n - \Delta_2} - \frac{\eta}{i \omega_n - \Delta_3}
\]

Here, \( \Delta_3 \) is the energy of the \( n + 1 \) to \( n + 2 \) transition, which is much above the Fermi level and can be ignored. As seen the equations above contain an unknown factor \( \eta \). This factor should be calculated from the Green function

\[
\eta = -\frac{1}{\pi} \sum_{\omega_{\nu}, \mathbf{k}} \text{Im} \left( G_{\nu} (\omega + i \delta, \mathbf{k}) f(\omega) \right).
\]

This equation has to be solved self-consistently, since the factor \( P \) renormalizes the Hamiltonian and overlap.

The corrections has been implemented in a full potential linear muffin tin (FP-LMTO) method. For the lanthanides, the face centered cubic structure (fcc) cubic lattice was used. This was due to the simplicity to perform calculations with one atom per primitive cell. In our calculations we set the same criteria for convergence in \( k \)-point summation, self-consistency, basis set truncation etc. as is done in normal electronic structure calculations.
IV. RESULTS

We selected Ce, Pr, Nd and Sm as elements of special interest to test our theory for, since we, in a previous work showed that the many-body effect of the upper transition is largest for them. The renormalizing factor, $\sqrt{P}$, is, according to our calculations, less than unity, and, thus, the mixing matrix elements are reduced somewhat. This means that the bandwidth is reduced compared to that obtained from a regular ESC. The upper transition can be taken from experiment, when available, or alternatively calculated from a constrained total energy calculation. In the present investigation we also made a scan, changing $\Delta_2$, from a position high above the Fermi-level, to a place closer to the Fermi-level. The results of the ESC-ARF theory are shown in Fig. 2. In this figure, the top figure shows the volumes as a function of the position of the upper transition, $\Delta_2$. The central one, shows the f-occupation and the lower one shows the renormalization factor, $\sqrt{P}$, for Ce, Pr, Nd and Pm. We note that the renormalizing factor is quite close to unity for all cases which means that the effect of the correlations for these materials is quite small. Further, when the upper transition is lowered, the f-occupation increases, and there is a contribution to the cohesive energy from the f-electrons, that results in that the volume decreases. In Table II we list the volumes for the selected lanthanides.

| element | Expt. $^a$ | LDA $^b$ | here |
|---------|---------|---------|------|
| Ce      | 3.8115  | 3.8994  | 3.7485 |
| Pr      | 3.8178  | 3.8375  | 3.9030 |
| Nd      | 3.8045  | 3.7848  | 3.7484 |
| Pm$^c$  | 3.7832  | 3.7415  | 3.5182 |

$^a$TABLE II. Volumes, $R_{SWS}$, for the light lanthanides, in a.u. When the position of the upper transition, $\Delta_2$ is put to the experimental value shown in Table I $^b$

$^b$Taken from ref. 9.

$^c$ESC with the 4f treated as core electrons.

$^c$Pm is radioactive, this value is a fit between Nd and Sm.

In Fig. 2 the density of states after the self-consistent cycle is shown. The occupied part of the d-band is quite similar for the case of a normal calculation treating the f-level as part of the core. Also, the 4f-band like feature is rather similar to what would be obtained from a regular ESC calculation, with a small narrowing due to the renormalization and a shift to higher energies, so that the number of f-electrons occupying this feature is small, $\sim 0.05-0.1$. The resulting electronic structure of our ESC-ARF theory is actually rather similar to that obtained when including Hubbard-Kanamory interactions to an LDA Hamiltonian (or the related LDA+U method) and to what is obtained from calculations including self-interaction corrections.

In Fig. 4 the f-bandwidth as a function of the position of the upper transition with respect to the Fermi level is plotted. The circles correspond to a self-consistent calculation where $\sqrt{P}$ is put to 1 during the whole cycle. The boxes are the result from a full calculation including all renormalization effects described above. A band narrowing effect is seen when $\sqrt{P} \neq 1$, but one may note that the effect is not extremely pronounced for the presently studied elements. One may speculate that for other systems, where a larger population of the upper level is expected (say, the level $\Delta_2$ is much closer to Fermi energy), the renormalization is more pronounced. Since the present modifications are similar to those presented for $\delta$-Pu $^{10}$, that does show a larger population of the upper band, it may very well be so that the present corrections are most important for this element.

V. CONCLUSION

We have presented a method to incorporate strong correlations into electronic structure calculations (ESC-ARF) and performed numerical tests of the theory. The results show a narrowing of the 4f-bands compared to LDA (or GGA) results. Due to the division of the 4f-states in a higher and lower level, we find that the cohesion from the 4f-states is non-zero (in contrast to calculations that treat the 4f-states as core states) but substantially smaller than what it would have been in an LDA (or GGA) calculation.

The present results are rather similar to our previous calculations, that include modifications in an LMTO-ASA method, although the full-potential treatment does include finer details of the potential. Due to the generalization of the corrections to an electronic structure method, that can treat any crystal structure, we believe the present method should have a potential in calculating the electronic structure of f-based materials that are hard to treat in a regular LDA (or GGA) ESC methods.
VI. ACKNOWLEDGMENTS

We are thankful for financial support from the Swedish Natural Science Research Council (NFR and TFR), for the foundation for strategic research (SSF) and the Göran Gustafsson foundation. J.M. Wills are acknowledged for supplying the codes for the FP-LMTO calculations.

1 U. Lundin, I. Sandalov, O. Eriksson, and B. Johansson, Physica B 259-261, 231 (1999).
2 U. Lundin, I. Sandalov, O. Eriksson, and B. Johansson, Sol. State Commun. 115, 7 (1999).
3 I. Sandalov, O. Eriksson, and B. Johansson, Preprint.
4 I. Sandalov, U. Lundin, and O. Eriksson, Preprint.
5 U. Lundin, I. Sandalov, O. Eriksson, and B. Johansson, Sol. State Commun. 115, 7 (2000).
6 Y. Baer and W. D. Schneider, Handbook on the Physics and Chemistry of the Rare Earths 10 (North-Holland, Amsterdam, 1987).
7 J. Wills, O. Eriksson, and M. Alouani, in ”Electronic Structure and Physical Properties of Solids”, ed. by H. Dressey ((Springer Verlag, Berlin, 2000)).
8 J. Wills and B. Cooper, Phys. Rev. B 36, 3809 (1987).
9 K. G. Jr, Bulletin of Alloy Phase Diagrams 11, 216 (1990).
10 O. Eriksson, D. Becker, J. Wills, and S. Balatsky, J. Alloys and Comp. 287, 1 (1999).

FIG. 1. The Hamiltonian (and overlap) matrix modified according to the text. $\Delta_2$ is the position of the upper transition.

FIG. 2. The volumes, f-occupation and $\sqrt{P}$-factor for Ce, Pr, Nd and Pm, as a function of the position of the upper transition, $\Delta_2$.

FIG. 3. The $d$- and $f$-projected density of states for the two cases when there are f-states in the valence basis with all corrections described above, and when a normal ESC with the $f$-electrons treated as core.

FIG. 4. The bandwidth of the $f$-states, when the renormalizing factor is put to one and when it is not.
