Theory of Strongly Correlated Electron Systems.
II. Intersite Coulomb Interaction and the Approximation of Renormalized Fermions in Total Energy Calculations.

I. Sandalov\textsuperscript{1,2}, U. Lundin\textsuperscript{1}, O. Eriksson\textsuperscript{1}
\textsuperscript{1}Condensed Matter Theory group, Uppsala University, Box 530, SE-751 21 Uppsala, Sweden
\textsuperscript{2}Dept. of Physics, Linköping University, SE-581 83 Linköping, Sweden

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The strong-coupling perturbation theory (SCPT) for correlated electron systems is extended to the case of full Coulomb interaction. The Coulomb mechanism of the orbital polarization is discussed and attention is paid to the importance of spectral weight transfer between the localized and delocalized subsystems of electrons. A one-to-one correspondence between subsets of Feynman graphs of SCPT (which we name the approximation of renormalized Fermions (ARF)) and weak-coupling perturbation theory (WCPT) is established. The comparison of the Galitskii and Migdal expression for the total energy and the Sham equation (which connects the self-energy and the exchange-correlation potential in density functional theory) for WCPT with the ones for the systems with strong electron correlations is used for the formulation of a simple theory for extending the local density approximation to density functional theory (DFT) to include explicitly correlations. The extension requires the inclusion of the many-electron spectral weights in the definition of the charge density and the renormalization of the mixing and hopping matrix elements caused by many body effects.

I. INTRODUCTION

The standard model of the lanthanides successfully explains most of magnetic properties and, within \textit{ab initio} calculations, also the equilibrium lattice parameter, bulk moduli and cohesive energy; actually, the picture of localized f-electrons works much better for compounds with rare earths than the picture of fully delocalized f-electrons. Nevertheless, it is not sufficient for an explanation of all the complex physical and chemical properties. A recent example is given in the neutron scattering experiment on Pr metal\textsuperscript{1}. The mechanism which can provide the f-localization, has been recognized long ago as the intra shell Coulomb interaction, which forms large energy gaps between occupied and unoccupied d- or f-orbitals. It has been explained within Hartree-Fock approximation by Brandow\textsuperscript{2} in connection with physics of Mott insulators and explicitly exploited in such phenomenological theories, as LDA+U, self-interaction corrected LDA DFT\textsuperscript{3,4}. It is clear that this picture is a bit oversimplified, since in many cases it is difficult to describe a local subsystem of materials within a single-electron approach. LDA-DFT is not a single-electron theory since it goes beyond the Hartree-Fock approximation at least up to the random phase approximation (RPA). However, it is also well-known that without formation of an energy gap with the help of SIC or LDA+U between f(d)-orbitals it is difficult to obtain electron localization in practical implementations of DFT.

However, in total energy calculations within the local density approximation to density functional theory, it is possible to treat the f-electrons either as core (or valence) electrons, obtaining localized states. Irrespective of if the f-states are localized or delocalized, there is a problem of taking into account strong correlations between f-electrons of non-filled shells, since the expression for the exchange-correlation potential usually is based on the expression derived from the theory for \textit{homogeneous} electron gas. The treatment of f-electrons as core states also requires a prescription of how many of them should be forced to be localized in the core. Even though the total energy may may be minimized with respect to the f-occupation\textsuperscript{6} this approach must rely on experimental data of the f-shell and it has problems of including fluctuations or non-integral occupations of the f-states. A theoretical method that attempts to describe all the intricate properties of f- (and d-) electron materials, such as heavy Fermion behavior, Kondo effects, Mott insulators (with a transition from a metal to insulator), unconventional super-conductivity, hybridization gaps etc., must be build on a many body framework, and it seems that a fruitful way to do this is to join many body corrections and electronic structure methods. The main motivation for this combination is that the many body theory described accurately the correlated f- (sometimes d-) states, whereas electronic structure methods treat the diffuse, more extended states well.

Here we suggest to look at the problem using a theory of strongly correlated electrons (SCE). We would like to combine field-theoretical methods with DFT. For the electrons which are localized the approach starting from
the atomic limit seems to be appropriate. The derivation of the connection between DFT and many-body theory for the total energy, given by Sham\cite{sham}, uses the expression for the total energy,\footnote{\textit{Phys. Rev.} B\textbf{7}, 488 (1973).} which contains the sum of all skeleton graphs. The theory of SCE from the atomic limit is based mainly on the Pauli-principle (e.g. for destruction operators $c_{f\sigma}^\dagger = 0$). Since some infinite sequence of graphs of perturbation theory from the weak-coupling side (say, for the self-energy for the Fermion Green function (GF)) corresponds to the expression where the relation like $n_{fa\sigma}^2 = n_{f\sigma}^x$ has been used within the strong-coupling perturbation theory, it is not easy to find this sequence and provide a one-to-one correspondence between these perturbation theories. It is possible, however, to express the Fermion GFs in terms of GFs for many-electron operators. Here we will exploit this connection.

The description within the framework of the LDA to DFT, when the $f$-electrons are treated as core electrons with only a certain number of $f$-orbitals occupied may be provided within the many-body approach in the following way. Let us consider an ion which has $n$ $f$-electrons in the ground state number. Then, only the transitions $\Gamma_n \rightarrow \Gamma_{n \pm 1}$ will be involved in the formation of the spectrum of the \textit{single-electron} excitations while all other transitions, like $\Gamma_n \rightarrow \Gamma_{n \pm 2}, \Gamma_{n \pm 3}$, involving larger number of electrons will be strongly suppressed by a large energy separation between these states. If we, in such theory, take the limit when the energy of the atomic-like transition $\Delta_2 \equiv E_{\Gamma_n}^{(n+1)} - E_{\Gamma_n}^{(n)}$ between any $n+1$ and $n$-electron states $\Gamma$ and $\Gamma'$ of the $f$-ion is much higher than the Fermi energy, $\varepsilon_F$, the number of $f$-electrons in the ion will be fixed. Indeed, in this limit this upper "single-electron" level $\Delta_2$ is empty. In the rare earth elements the populated part of the $f$-spectral density corresponding to the $\Gamma_n \rightarrow \Gamma_{n \pm 1}$ transitions is sometimes only slightly above Fermi energy. Therefore, due to mixing interaction it should contribute to the cohesive energy.\footnote{\textit{Phys. Rev.} B\textbf{8}, 179 (1973).} The total energy of the system and Fermion GFs can be calculated in simple approximation by making use of the theory developed in Ref.\cite{sham}. This allows to construct the Sham equation for the exchange-correlation potential and to derive corrections to the standard LDA expression.

The paper is organized as follows. In Section II, in order to provide an opportunity to directly compare the contributions from Coulomb interaction to the equations of motion for GFs in WCPT and SCPT, the equations of motion are written exactly via functional derivatives of the GFs in WCPT (see Section II A) and in SCPT (see Section II B) within a real-space non-orthogonal representation. Here we introduce the approximation of renormalized Fermions (ARF), which allows us to establish a one-to-one correspondence between certain subsequences of graphs in WCPT and SCPT. This fact is used further for the formulation of an recipe for a correlation corrected form of LDA on the basis of the analysis by Sham\cite{sham} for the exchange-correlation potential for a normal and a correlated system. In Section III we discuss the standard model for the lanthanides and compare the self-energies within WCPT and SCPT in the ARF. Since the graphs which are not taken into account by this approximation can be written explicitly, this allows us to establish the domain of validity of the standard approach to the case when the system has (quasi)localized electrons, and, also, suggests a possible recipe to overcome the difficulties existing in the LDA in DFT. Section IV contains the conclusions and a discussion. The contributions to the equations of motion for the GFs are rewritten via functional derivatives of GFs. This allows to construct a regular SCPT via an iteration procedure for the equations for the GFs. In Appendix B we discuss the transfer of spectral weight between the low and high energy regions and show the role played by spectral weights in the formation of the orbital polarization in the simple example of 3-orbital atoms with 2 strongly interacting electrons.

II. COULOMB INTERACTION AND GREEN FUNCTIONS

A. WCPT for an Non-Orthogonal Set

Perturbation theory from the atomic limit should, on one hand, be constructed in real space in order to be able to treat the single-site Coulomb interactions better than within the LDA. The wave functions centered on different atoms are not supposed to be orthogonal to each other. On the other hand, we have to compare the perturbation series for the GFs within weak coupling and strong coupling. For this reason we have to understand how the equations reflect the non-orthogonality of the basis set. Here, we shortly repeat the well-known Kadanoff and Baym derivation for the exact expression for the self-energy and obtain the first corrections which we will compare with the ones obtained.
from the SCPT approach later. First we have to introduce the $S$-matrix with an external field $U_{23}(t)a^\dagger_{a3}a_{a5}$ Then, for the Hamiltonian

$$H = h^0_{23}a^\dagger_{a3}a_{a3} + \frac{1}{2} v_{2345}a^\dagger_{a2}a_{a3}a_{a4}a_{a5},$$

(1)

where $h^0_{23} = (2\frac{e^2}{2\pi\varepsilon} + v(r))$ and $v_{2345}$ is a matrix element of the Coulomb interaction, the equation of motion for the GF $F_{11'}(t, t')$ has the form: (the letter $F$ will be used for Fermonic GFs below keeping $G$ for the GFs involving Hubbard operators)

$$\{\delta_{13}i\partial_t - O^{-1}_{12}[\hat{h}^0_{23}(t) - v_{\sigma,23}^\dagger]\}F_{11'}(t, t') = i\delta(t - t')O^{-1}_{11'},$$

$$+ O^{-1}_{12}v_{[23]45}(\hat{T}a^\dagger_{a1}(t)a_{a5}(t)a^\dagger_{a2}(t'))U,$$

(2)

where $v_{[23]45} = \frac{1}{2}(v_{2345} - v_{3245})$, $\hat{h}^0_{23} = h^0_{23} + U_{23}(t)$ and the notation $U$ in the GF $F_{11'}(tt'|U)$ means that it satisfies the equation of motion in the external field $U$. The boundary conditions for GFs are based on cyclic permutations of operators under sign of trace and, therefore, are not changed by the non-orthogonality.

The Dyson equation for the full GF,

$$\{\delta_{13}i\partial_t - O^{-1}_{12}\int dt_1[\hat{h}^0_{23}(t)$$

$$- v_{\sigma,23}^\dagger]\delta(t - t_1) - \Sigma_{23}(t, t_1|U)]\}F_{11'}(t, t') = i\delta(t - t')O^{-1}_{11'},$$

(3)

can be written if we write the double-electron GF via a functional derivative

$$\langle T a^\dagger_{a3}(t)a_{a4}(t)a_{a5}(t)a^\dagger_{a2}(t')\rangle_U = [F_{34}(t, t^+|U)$$

$$- \frac{\delta}{\delta U_{34}(t^+)} F_{51'}(t, t'|U)\},$$

(4)

and define the self-energy as

$$\Sigma_{21'}(t, t'|U) = \{v_{[23]45} [F_{34}(t, t^+|U) +$$

$$\frac{\delta}{\delta U_{34}(t^+)} F_{56}(t, t_1|U)]\} F_{11'}^{-1}(t, t'|U).$$

(5)

Here, the inverse of the GF is defined by the equations

$$F_{56}(t, t_1|U)F_{61'}^{-1}(t_1, t'|U) = F_{56}^{-1}(t, t_1|U)F_{61'}(t_1, t'|U)$$

$$= \delta(t - t')\delta_{11'}.$$

(6)

The Hartree correction appears if we neglect the functional derivative in the self-energy

$$\Sigma^{H}_{21'}(t, t_1|U) = v_{[23]45} F_{34}(t, t^+|U),$$

(7)

and the Fock correction comes from the derivative $\delta F^0/\delta U$:

$$\Sigma^{F}_{21'}(t, t_1|U) = - v_{[23]45} F_{53}(t, t^+|U).$$

(8)

As we see, the first-order corrections to the self-energy do not contain the overlap matrix. The next corrections do not contain it either. We will also need the RPA-screened Coulomb interaction. The difference between the standard procedure for Fermions and the one in this representation consists only in the necessity to write the representation indices. Introducing the effective field

\[\text{\footnotesize \textsuperscript{1}The external field } U_{23} \text{ should not be confused with the Hubbard } U\]
\[ U_{21}^{\text{eff}}(t) = U_{21}'(t) + \Sigma_{21}'(t) \]  

and \( \Sigma' = \Sigma - \Sigma^H \) we can rewrite \( \Sigma' \) in terms of \( U^{\text{eff}} \) as follows:

\[
\Sigma_{21}'(t, t'|U) = v_{[23]45} \frac{\delta U_{78}^{\text{eff}}(t_2)}{\delta U_{78}^{\text{eff}}(t_2)} \frac{\delta F_{56}(t, t_1|U)}{\delta F_{61'}(t_1, t'|U)} F_{61'}^{-1}(t_1, t'|U) 
= \tilde{v}_{2785}(t_2, t^+) \frac{\delta F_{56}(t, t_1|U)}{\delta U_{78}^{\text{eff}}(t_2)} F_{61'}^{-1}(t_1, t'|U) 
= \tilde{v}_{2785}(t_2, t^+) F_{59}(t, t_3|U) \frac{\delta F_{61'}^{-1}(t_0, t'|U)}{\delta U_{78}^{\text{eff}}(t_2)}. \]

The effective interaction, \( \tilde{v} \), is

\[
\tilde{v}_{2785}(t_2, t^+) \equiv v_{[23]45} \frac{\delta U_{78}^{\text{eff}}(t_2)}{\delta U_{78}^{\text{eff}}(t_2)} \equiv v_{[23]45} \varepsilon_{78,34}^{-1}(t_2, t^+). \]

Using the zero approximation for the vertex \( (F^{-1} \to F_0^{-1}) \)

\[
\frac{\delta F_{61'}^{-1}(t_0, t'|U)}{\delta U_{78}^{\text{eff}}(t_2)} \simeq -\delta(t_0 - t') \delta(t_2 - t') \delta t_0 \delta t \]

we obtain the desired expression for self-energy in RPA:

\[
\Sigma_{21}^{\text{RPA}}(t, t'|U) = -\tilde{v}_{2710}(t', t^+) F_{57}(t, t'|U). \]

The inverse of the dielectric permeability, \( \varepsilon^{-1} \), entering the effective interaction is determined by the equation:

\[
\varepsilon_{71',34}^{-1}(t', t^+) = \delta(t^+ - t') \delta t_0 \delta t + v_{[73]41'} F_{35}(t, t_0|U) F_{64}(t_0, t^+|U) \varepsilon_{56,34}^{-1}(t', t^+). \]

Putting the external fields \( U = 0 \) and making a Fourier transformation with respect to time we find the equation in terms of Matsubara frequencies (below we use \( i \omega \) for Fermionic and \( i \Omega \) for Bosonic frequencies)

\[
\varepsilon_{71',34}^{-1}(i\Omega) = \delta t_0 \delta t + v_{[73]41'} \Pi_{35,64}^0(i\Omega) \varepsilon_{56,34}^{-1}(i\Omega), \]

where

\[
\Pi_{35,64}^0(i\Omega) \equiv T \sum_{\omega} F_{35}(i\omega) F_{64}(i\omega + i\Omega). \]

Then, the self-energy \( (U = 0) \) is

\[
\Sigma_{21}^{\text{RPA}}(i\omega) = -v_{[23]45} T \sum_{\omega_1} \varepsilon_{71',34}^{-1}(i\omega - i\omega_1) F_{57}(i\omega_1). \]

Let us write it as sum of "static" and "dynamic" parts:

\[
\Sigma_{21}^{\text{RPA}}(i\omega) = \Sigma_{\text{st,21}'}^{\text{RPA}} + \Sigma_{\text{dyn,21}'}^{\text{RPA}}(i\omega), \]

where

\[
\Sigma_{\text{st,21}'}^{\text{RPA}} = -v_{[23]45} \varepsilon_{71',34}^{-1} T \sum_{\omega_1} F_{57}(i\omega_1) = \varepsilon_{21'}^{(ex)}, \]

\[
\Sigma_{\text{dyn,21}'}^{\text{RPA}}(i\omega) = -v_{[23]45} T \sum_{\omega_1} \varepsilon_{71',34}^{-1}(i\omega - i\omega_1) 
- \varepsilon_{71',34}^{(ex)} F_{57}(i\omega_1). \]
Here we separated the frequency-independent part of the dielectric permeability $\varepsilon_{\gamma}^{\text{ret}}$. Its contribution to the self-energy, $\Sigma^{\text{RPA}}_{\gamma}$, which is the frequency-independent part of the screened exchange interaction, is denoted $\nu_{\gamma}^{(\text{ex})}$. The formulas given above have to be compared with the corresponding expressions in SCPT. We will see below that in SCPT $f$- and non-$f$-electrons are renormalized differently, for this reason we will need these formulas in terms of $f$- and non-$f$ indices ($c$) separately. Each of the corrections, say, $\Sigma^{\text{RPA}}$, $\Sigma^{\text{RPA}}^{\text{H}}$, $\Sigma^{\text{RPA}}^{\text{F}}$ contains four terms since each index takes two values: $1 = (c, f)$, where $c = (j L)$ and $f = (j \mu)$.

$$
\begin{align}
\Sigma^{\text{H}}_{jL, j'L'}(tt^+[U]) &= v_{jL, j'L'}(tt^+[U])
= v_{jL, j'L'}(tt^+[U]) \\
&+ v_{jL, j'L'}(tt^+[U]) \\
&+ v_{jL, j'L'}(tt^+[U]) \\
&+ v_{jL, j'L'}(tt^+[U]),
\end{align}
(21)
$$

$$
\begin{align}
\Sigma^{\text{RPA}}_{jL, j'L'}(tt'[U]) &= -[\tilde{v}_{jL, j'L'}(tt'[U])] \\
&+ \tilde{v}_{jL, j'L'}(tt'[U]) \\
&+ \tilde{v}_{jL, j'L'}(tt'[U]) \\
&+ \tilde{v}_{jL, j'L'}(tt'[U]),
\end{align}
(22)
$$

Thus, we can conclude, that within WCPT the overlap matrices enter only the equations via the definition of the zero GF. As we shall soon see, the situation is more complex within SCPT, since in this case, the overlap matrices enter in a form combining the inverse of the overlap matrix with many-electron population numbers. In the case when we take into account only the static part of the screening, the formula for the total energy can still be written in a simple form. Let us write it on the basis of Eq. (30). Let us denote the Hartree part of the Hamiltonian as

$$
h_{12}^{\text{H}} = (1|h_{12}^{\text{H}}(r)|2) = (1|\frac{p^2}{2m} + v_{\text{ne}}(r) + v_{\text{H}}^{\text{ex}}(r)|2).
(29)
$$

Then, representing the overlap matrix in the Cholesky form, $O_{12} = Z_{12}Z_{21}$, and introducing the eigenvectors, $u^{\gamma}_\alpha$, and eigenstates, $\varepsilon^{\gamma}$, by the equation

$$
\sum_{12\delta} Z_{1\delta}^{-1}[h_{12}^{\text{H}} + v_{12}^{(\text{ex})}]Z_{2\delta}^{-1} : u^{\gamma}_\alpha = \varepsilon^{\gamma}u^{\gamma}_\alpha.
(30)
$$

We see that the solution to the equation for the GF in this approximation,

$$
(\{O_{12}\omega - [h_{12}^{\text{H}} + v_{12}^{(\text{ex})}]) F_{21}\omega = \delta_{11'},
(31)
$$

can be written in the following form

$$
F_{12} = \langle \langle a_1 | a_2^\dagger \rangle \rangle^{(\text{ret})}_{\omega} = \sum_{\alpha\gamma\nu} \tilde{Z}_{1\gamma}^{-1} u^{\gamma}_\alpha u^{\nu}_\alpha Z_{\alpha\gamma}^{-1} \omega - \varepsilon^{\gamma} + i\delta.
(32)
$$

Then, the expectation value $\langle a_1^\dagger a_1 \rangle$ is given by

$$
\langle a_1^\dagger a_1 \rangle = \sum_{\alpha\gamma\nu} \tilde{Z}_{1\gamma}^{-1} u^{\gamma}_\alpha f(\varepsilon^{\nu}) u^{\nu}_\alpha Z_{\alpha\gamma}^{-1}.
(33)
$$

The charge density $\rho(r)$ can then be written as follows

$$
\rho(x) = -i \lim_{\omega \rightarrow x} \sum_{12} \phi_1(x) \sum_{\omega} e^{i\omega x} F_{12}(i\omega) |\phi_2^+(x')
= \sum_{12} \phi_2^+(x') \phi_1(x) |a_2 a_1\rangle
= -i \lim_{\omega \rightarrow x} \sum_{12} \phi_1(x) \sum_{\omega} e^{i\omega x} F_{12}^{\text{DFT}}(i\omega) |\phi_2^+(x')
= \sum_{12} \phi_2^+(x') \phi_1(x) |a_2 a_1\rangle^{\text{DFT}}.
(34)
$$

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Further, we can use the Migdal-Galitskii expression for the total energy, written in terms of, say, retarded Fermion Green functions,

$$E_{tot} = \frac{1}{2} \int d\omega [O_{12}\omega + (h_{12}^0 - v_{12}^{el})]f(\omega)(-\frac{1}{\pi})$$

\[ \times \text{Im} F_{12}(\omega + i\delta). \]  (36)

In order to avoid possible confusion we note that $F_{12}(i\omega)$ are the coefficients of expansion of the GF in a series of the functions $\phi_{jL}(r)$,

$$F(r, t; r', t') = \frac{1}{i} \langle T \psi(r, t) | \psi^\dagger(r, t') \rangle = \sum_{12} \phi_1(x) F_{12}(i\omega) \phi_2(x')$$  (37)

and they do not coincide with the matrix elements $\tilde{F}_{12}(t, t') = \int dr' \phi_1^\dagger(r) F^{(ret)}(r, t; r', t') \phi_2(r)$ calculated on this functions.

Inserting the imaginary part of the GF, Eq.(32), into the expression for total energy, Eq.(36), we find within the static RPA

$$E_{tot}^H = \frac{1}{2} \sum_{12\gamma} \bar{Z}_{12\gamma}^{-1} u_\gamma^\nu (O_{12} \varepsilon^\nu + (1 - \frac{p^2}{2m} + v_{ne}(r)|2])$$

\[ \times f(\varepsilon^\nu) u^\nu_\alpha Z_{\alpha1}^{-1} \]

\[ = \frac{1}{2} \left\{ (1 - \frac{p^2}{2m} + v_{ne}(r) + v^H(r)|2 - v_{12}^{ex}) \right\} \]

\[ + \frac{1}{2} \left\{ \int dr |\psi_\gamma(r)| \frac{p^2}{2m} + v_{ne}(r) |\psi_\gamma(r)\right\} \]

\[ + \int dr \int dr' \rho(r) \rho(r') \theta_{12}^{ex}(a_1^\dagger a_2) \right\}, \]  (38)

as expected. As follows from the comparison of the standard Kohn-Sham expression for total energy used in DFT calculations, the term $v_{12}^{ex}(a_1^\dagger a_2)$ should be identified with the term $\int \rho(r) \upsilon_{12}^{ex}(r)$ in DFT, i.e. with the contribution to the total energy from the screened exchange potential. According to Kotani\cite{Kotani}, this expression in a static approximation ($\omega = 0$) should give (at least, for normal metals) values close to what is usually obtained within standard LDA DFT calculations.

One can write the expression for $E_{tot}$ also for the case of frequency-dependent screening. Then the self-energy also depends on frequency. For this case one can apply the idea of Migdal\cite{Migdal} to introduce energy dependent eigenfunctions in order to diagonalize the GF

$$\sum_{12\gamma} Z_{12\gamma}^{-1} \bar{Z}_{2\gamma}^{-1} \cdot u_\gamma^\nu (\omega) = E^\nu (\omega) u_\gamma^\nu (\omega).$$  (41)

Then, the Fermion GF is

$$F_{12}^{(ret)} = (\langle a_1 | a_2^\dagger \rangle)^{(ret)} \omega = \sum_{\alpha\gamma\nu} Z_{1\gamma\nu}^{-1} u_\gamma^\nu (\omega) Z_{\alpha1}^{-1} \omega - E^\nu (\omega) + i\delta.$$  (42)

The spectrum of the single-particle excitations is then determined by the poles of the GF

$$\varepsilon^\nu = E^\nu (\varepsilon^\nu),$$  (43)

where

$$E^\nu (\varepsilon^\nu) = u_\gamma^\nu (\varepsilon^\nu) Z_{1\gamma}^{-1} \bar{Z}_{2\gamma}^{-1} \cdot u_\gamma^\nu (\varepsilon^\nu).$$  (44)
In turn, the total energy acquires the form
\[
E_{\text{tot}} = \frac{1}{2} \sum_{12\gamma\alpha} \bar{Z}_{2\gamma}^{-1} u_\gamma^a(\varepsilon_\nu^\prime) \left[ O_{12} \varepsilon_\nu^\prime + \left( 1 + \frac{\bar{u}_{\gamma}^a(r)}{v_{\text{ext}}(r)} \right) \right]_\nu^\prime \\
\times f(\varepsilon_\nu^\prime) u_\alpha^\gamma(\varepsilon_\nu^\prime) Z_{\gamma m}^{-1}.
\]
(45)

Thus, the eigenvectors \( u_\gamma^a(\varepsilon_\nu^\prime) \) are needed only at \( \omega = \varepsilon_\nu^\prime \) and the renormalization factor \( \left[ 1 - \left( \frac{\partial E_\nu}{\partial \omega} \right)_{\varepsilon_\nu^\prime} \right]^{-1} \) takes into account the correlation induced deviation of the distribution function from a purely Fermionic one.

At last, we have to note that in the case when one takes into account also the decay of the quasi-particles, the total energy can be calculated directly from Eq. (36).

The facts which we are going to exploit further are: 1) the Galitskii-Migdal formula, Eq. (36), gives the total energy in the approximation chosen for Fermionic GFs; 2) the Fermionic GFs can be expressed in the form of a linear combination of the GFs for the Hubbard operators; 3) the lower intra atomic Fermi-like transitions give only core-like contribution to the energy. The latter statement will be considered in the next section. In the region of strong intra atomic coupling, the self-energies \( \Sigma_{j\mu,j\prime\nu'}, \Sigma_{j\mu,j'L} \) for Fermionic GFs also can be found for many cases by making use of the SCPT where a non-perturbative calculation should be used for the interaction between electrons in each ion, but perturbative ones with respect to the interactions connecting different ions. How to calculate the GFs for Hubbard operators is discussed in next subsection and the details are given in Appendix A.

### B. SCPT and the Approximation of Renormalized Fermions

If the Hubbard intra atomic repulsion is strong enough the perturbation theory from the atomic limit generates the following physical picture. The partially filled \( d \)- (or \( f \)-) shell is separated by a large energy gap to two subs hells. One of them can be viewed as core-like states, while the other one can, in a certain approximation, be described in terms of effective, renormalized, Fermions. These quasi-Fermions behave very similar to the Fermions in the weak-coupling regime. However, this simple picture arises only within the lowest approximation where the upper Hubbard sub bands are similar to the corresponding sub band of the so-called Hubbard-I approximation in the Hubbard models and the decay of the quasi-particles is only due to normal scattering of these quasi Fermions caused by Coulomb intersite interaction. The scattering on collective excitations like spin waves, etc., as well as the scattering caused by kinematic interactions, is not taken into account.

In this case the Fermi-liquid type of decay (\( \sim T^2 \)) still holds at low temperature and excitation energy. Our aim will be to show that, in the \( ab \text{ initio} \) calculations, for materials where the strong correlations are not developed very much due to the suppression by the a strong localization of a part of a shell, one can use the standard expression for the exchange-correlation potential even in the case of strong electron correlations (SEC) with the difference that a modified expression for the charge density should be used and, also, hopping, mixing and overlap matrixes should be slightly renormalized. In general case the renormalization constants, however, cannot be found without the system of equations for the GFs derived within SCPT. After some simplifying assumptions only one constant enters the equations and, therefore, only one equation should be added (see next paper).

The idea of the derivation performed consists of the following. The density functional theory is based on an self-consistent solution of the Kohn-Sham equations for the charge density and potential. The key question is, of course, from where does one take the analytical form for this potential. Usually it is taken from the theory of the homogeneous electron gas and phenomenologically extended to the case of non-homogeneous systems. Sham\(^2\), using the Hohenberg and Kohn theorem\(^3\), has suggested a theory which connects the exact exchange-correlation potential with the exact self-energy. Although it is far from obvious that the same holds for the case of an approximate self-energy, we will use this assumption. Sham and Schlüter\(^4\) managed to solve this equation for the case of semiconductors within the approximation of spherical charge spheres and found that the analytical form in this approximation is the same as in the case of an phenomenological extension of the theory of homogeneous gas. At last, Kotani\(^5\) has shown that the results of the standard DFT-LDA calculations for the total energy are well reproduced within the static random phase approximation (RPA). These facts can be used as follows. If we manage to

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\(^2\)Although Hubbard did not consider in his works the inter-site Coulomb interactions, the approximation we use has the same underlying physics and, therefore, we will use the same name "Hubbard-I" for this approximation.
1. establish a one-to-one mapping between a subset of the Feynman graphs for the self-energy within SCPT and WCPT (at least, in RPA) and
2. show that the Sham equation for the exchange-correlation potential within this subset of graphs has the same form as its analogue in WCPT and
3. derive the expression for the charge density \( \rho_P(r) \) within the approximation in the SCPT, which is the analogue of the RPA in WCPT,

then, the analytical form for the exchange-correlation potential in this approximation should be the same as in the standard case, but the usual expression for the charge density \( \rho(r) \) should be changed to \( \rho_P(r) : \psi_{xc}[\rho_P(r)] \rightarrow \psi_{xc}[\rho_P(r)] \), as well as the matrix elements of different interactions should be renormalized as it is required by the mapping. Since the LDA for the exchange-correlation potential works well for the case of delocalized electrons, we, thus, have to show that any graph in WCPT describing the Coulomb interaction between the electrons which belongs to one site and the other either to another site, or to the delocalized states, has its counter-part in the SCPT. As follows from the formulas for total energy and the Sham equation, both require knowledge of the full Fermionic GFs. Therefore, we have to derive the equations for the GFs, \( G \), constructed in \( X \)-operators and, then, express the Fermionic GF, \( F \), in terms of GFs \( G \).

In the SCPT the \( f \)-electron operator can be expressed in terms of Fermion-like intra-atomic excitation. In the approximation Hubbard-I (HIA) the latter can be described in terms of renormalized electrons. The mapping looks as follows

\[
v^{Coul} \cdot \hat{f}_\mu = v^{Coul} \cdot f_\mu \hat{X}^a \Rightarrow (v^{Coul} \sqrt{P^a}) \cdot f_\mu (\hat{X}^a \sqrt{P^a}).
\]

where \( \hat{f}_a \) is the operator of an effective Fermion, and \( P^a \) is the spectral weight. Formally, this approximation can be obtained by a simple exchange of the commutation relations

\[
\{X^a, X^b\} = \epsilon^{ab}_\xi Z^\xi = \epsilon^{ab}_\xi (Z^\xi) + [\epsilon^{ab}_\xi Z^\xi - \epsilon^{ab}_\xi (Z^\xi)]
\]

\[
\approx \epsilon^{ab}_\xi (Z^\xi),
\]

\[
\{c_1, X^b_{j_2}\} \approx O^{-1}_{12} f^a_{j_2} \epsilon^{ab} / Z^\xi.
\]

Within the orbital representation where \( \epsilon^{ab}_\xi = \delta^{ab} \delta(\xi - [\Gamma, \Gamma]) \), i.e. it can only take the values 1, 0, and the matrix elements \( f^a_{j_2} = 1, 0, -1 \). The expectation value is non-zero only when it is one of the population numbers, \( \langle Z^\xi \rangle = \delta_{\xi,[\Gamma,\Gamma]} \langle \hat{n}^\Gamma \rangle = \delta_{\xi,[\Gamma,\Gamma]} N_\Gamma \); then

\[
\epsilon^{ab}_\xi (Z^\xi) = \epsilon^{ab}_\xi (\delta_{\xi,[\Gamma,\Gamma]} + \delta_{\xi,[\gamma,\gamma]}) \delta(a - b) P^a
\]

\[
\equiv \delta(a - b) [N_\Gamma + N_\gamma]
\]

for the transition \( a = [\gamma, \Gamma] \) and, therefore,

\[
\{c_1, X^b_{j_2}\} \approx O^{-1}_{12} f^a_{j_2} P^a_{j_2} \delta(a - b).
\]

Then, the \( X \)-operator can be written as \( X = (X^a \sqrt{P^a}) \sqrt{P^a} = \hat{f}_a \sqrt{P^a} \). Then, the interaction is renormalized by the square root of \( P \), which is brought by the \( X \)- (or, due to non-orthogonality of the basis set, c-) operator into the equation of motion for the GF and in the lowest approximations plays the role of the spectral weight of the pole, corresponding to the transition \( a \). If the fluctuations described by the GFs, \( \langle T[\epsilon^{ab}_\xi Z^\xi(t) - \epsilon^{ab}_\xi (Z^\xi)] [\epsilon^{ab}_\xi Z^\xi(t') - \epsilon^{ab}_\xi (Z^\xi(t'))] \rangle \), are neglected, the perturbation theory contains only Fermi-like Feynman graphs. The latter means that any Feynman graph obtained within a weak-coupling expansion has its counter-part in the strong-coupling perturbation theory. Attention has to be paid to the fact that the number of renormalized Fermions does not coincide with the number of ordinary Fermions: the number of the latter is equal to the number of orbitals involved, while the number of the former is equal to the number of Fermi-like transitions involved. Although it is not difficult in principle to answer the question, how to derive this approximation and what remains beyond this approximation, it requires quite lengthy calculations.

Different ways may be used for the calculation of the Fermionic GFs within the SCPT: 1) directly, either via a chain of equations of motion, until the chain becomes closed on one site via the operator relations \( f^2 = 0, [\hat{n}_\mu(f)]=[\hat{n}_\mu(f) \), or, equivalently, in terms of chain of high-order GFs; 2) using the representation of Hubbard operators, which diagonalize the on-site interactions, and the diagram technique for them. Then we have to find the Fermion-like GFs via the
Hubbard $X$-operators. Here we use the second way, since the SCPT for the GFs are needed and some approximations are considered in a paper by Sandalov et al. Let us inspect how the first-order corrections to GFs generated by the same types of the matrix elements of the Coulomb interaction look like (one should remember that the inverse of the overlap matrix is not included into the definition of self-energy).

The term of the Hamiltonian describing the Coulomb interaction between electrons can be written in the $jL$-representation in the form

$$H_{\text{Coul}} = \frac{1}{2}v_{2345}[\bar{c}_2^+ + (f_1^\dagger)^{34}X_{34}^a][c_4^a + (f_3^\dagger)^{45}X_{45}^a]$$

$$\times [c_4 + f_4^{a\dagger}X_{4}^{a\dagger}][c_5 + f_5^{a5}X_{5}^{a5}].$$

(51)

The interactions with the core electrons are included into the definition of the $X$-operators here. Now we have to consider all these sixteen terms in order to take into account single-site correlations via multiplication rules for the Hubbard operators. It is convenient to consider the terms which contain different number of $f$-operators separately. Thus, we form classes according to the number of $f$-operators contained in the interaction term. In order to reduce the number of terms in the equations of motion we collect similar terms by making use of the commutation relations and a proper symmetrization of the interaction. We also use the short-hand notations for indices: for conduction electrons $1_c = (j_1, l_1) \equiv (j_1, l_1 \neq 3, m_{1l}, s_1 = 1/2, \sigma_1)$ and for $f$-electrons $1_f = (j_1, \mu_1) \equiv (j_1, l_1 = 3, m_{1l}, s_1 = 1/2, \sigma_1)$, where it does not lead to a confusion. Also, it is convenient to introduce the group constants which are the coefficients in the multiplication rules for $X$-operators:

$$X_j^a \cdot X_j^b = \kappa_{\xi}^{ab}Z_j^\xi, \quad X_j^a \cdot Z_j^\xi = \kappa_{\xi}^{ba}X_j^b, \quad \text{etc.}$$

(52)

Obviously,

$$\epsilon_{\xi}^{ab} = \kappa_{\xi}^{ab} + \kappa_{\xi}^{ba}$$

(53)

and so on.

The $f$-operator in $X$-representation is given by a sum of $X$-operators, and we are not able to find the Fermionic GF $F(jf) = \langle T_{f_1}(\tau_1) f_1^\dagger(\tau_2) \rangle$ without finding the GFs $G^{xc}, G^{cc}, G^{XX}$, involving Hubbard $X$-operators. Therefore, we need the equations for these GFs. For the Hamiltonian which includes hopping and mixing interactions (Hubbard-Anderson model) these equations are given in a paper by Sandalov et al. Therefore, we have to add the terms generated by Coulomb interaction. If we write the equations in terms of functional derivatives with respect to the external field, all mixed terms arise when we iterate these equations. However, as seen from the form of the contributions from the Coulomb interactions to the equations of motion for the operators $c$ and $X$ (see Appendix A), the fields which are introduced in Ref. are not sufficient. Now instead of the $S_{\text{ext}}$-matrix, describing external fields we have to use the following $S_{\text{ext}}$:

$$S_{\text{ext}}(-i\beta, 0) = \exp \left\{ -i \int_0^{-i\beta} dt \mathcal{L}_{\text{ext}}(t) \right\},$$

(54)

where

$$\mathcal{L}_{\text{ext}}(t) = \sum_{jL} U^Z_{jL}(t) \bar{Z}^\xi(t) + \sum_{jL, j' L'} c_{jL}^\dagger(t)L_{jL, j'L'}(t)c_{j'L'}(t)$$

$$+ \sum_{jL, j' L'} c_{jL}^\dagger(t)L_{jL, j'a'}(t)c_{j'a'}(t)X_{jL}^a(t)$$

$$+ \sum_{jL, j' L'} X_{jL}^a(t)L_{jL, j'a'}(t)c_{j'a'}(t)$$

$$+ \sum_{jL, j' L'} X_{jL}^a(t)L_{jL, j'a'}(t)c_{j'a'}(t)(1 - \delta_{j' j}).$$

(55)

As seen, all terms except the one proportional to $U^Z_{jL}$ renormalize, the $c$-$c$-hopping of the conduction electrons, mixing and $f$-$f$-hopping:

$$\mathcal{H}^{cc} \rightarrow \tilde{\mathcal{H}}^{cc} = \mathcal{H}^{cc} + U^{cc},$$

$$W \rightarrow \tilde{W} = W + U^{cx},$$

$$t \rightarrow \tilde{t} = t + U^{cc},$$

(56)
therefore, we consider that all these external fields are included into hopping and mixing matrix elements below. These fields generate the terms already considered in a paper by Sandalov et al.\cite{54} in perturbation theory, and the problem has a non-linear nature from the very beginning. Now, using the contributions into the equations of motion from the Coulomb interaction, given in Appendix A, we will express the new complex GFs in terms of the simple ones. It is convenient to consider these contributions class by class; the number of the class corresponds to the number of \( f \)-operators in the term of Coulomb interaction. Before doing this it useful to note that contrary to the weak-coupling expansion the representation which we use here is not unique. However, after one is chosen, it generates the system of graphs of the diagram technique which corresponds to this choice of the closed form of the equations for the GFs since we obtain the graphs by means of iterations of these equations. As a consequence, special care is required in comparison with some other techniques: one should not expect graph-to-graph correspondence between different diagram expansions for the GFs. Our convention here is the following: in the first step we separate the first Bose-like operator which stands in the left-time product and then, if necessary, make it again. This sequence simplifies the calculation of the necessary time limits. The analogue of the Hubbard-I approximation (HIA) is obtained if one fully neglects all the contributions coming from the functional derivatives.

The approximation of “renormalized Fermions” can be introduced if

a) we will show that, from a physical point of view, the system of correlated electrons has the Fermion-like excitations, which may differ very little from the ones in an weakly interacting Fermions gas, at least in some region of parameters (strength of interactions, dimensionality, temperature, etc.);

b) from the point of view of mathematics we will show that even in the strong-coupling regime a subsequence of Feynman graphs in SCPT exists which describes these excitations. Then, the remaining graphs will determine the region of parameters where this approximation is valid.

We will now search for a solution to the equations of motion for the GFs in the form

\[
G = DP, \tag{57}
\]

where the bold letters denote matrixes with respect to all indices and times as well as their product implies matrix multiplication with respect to all indices. Here the GF is

\[
G_{\alpha \beta} = \frac{1}{\tau} \langle T \eta_{\alpha}(t) \eta_{\beta}(t') \rangle_U, \quad \eta_{\alpha}(t) = c_{jL}(t), X^a(t). \tag{58}
\]

The \( cc \)-component here \( G_{11} = G^{(cc)} \equiv F^{(cc)} \) is a Fermion GF. In terms of the operators \( \eta \), the interaction can be written as

\[
\tilde{V}_{\text{Coul}} = \frac{1}{2} \bar{v}_{2345} \eta_2^\dagger \eta_3 \eta_4 \eta_5, \tag{59}
\]

with

\[
\bar{v}_{2345}^{(cc)} = v_{j2} L_{2,3} L_{3,4} L_{4,5} L_5; \\
\bar{v}_{2345}^{(fc)} = v_{j2} L_{2,3} \mu_3 L_{4,5} (f_{\mu 3}^\dagger)^a; \\
\bar{v}_{2345}^{(ff)} = v_{j2} L_{2,3} \mu_3 \mu_4 L_{4,5} L_5 (f_{\mu 3}^\dagger)^a (f_{\mu 4}^\dagger)^a, \quad \text{etc.} \tag{60}
\]

The external fields in Eq.\,(54) and Eq.\,(55) can also be written shortly as \( \eta_3^b U_{34} \eta_4 \). Of course, the operators belonging to the same site should be multiplied according to the rules for the \( X \)-operators, Eq.\,(52). We shall consider these terms, later. Since the anticommutators \{\( c, X^\dagger \), \( \{X, X^\dagger \) \} give an operator, not \( c \)-number, we have to write all equations for a general case \( \{\eta_1, \eta_2\} = \varepsilon_{3_6}^{12} Z^{3b} \), where \( Z \) is Bose-like operator and, therefore, \( \tilde{V}_{\text{Coul}} \) gives the following contribution into the equations of motion

\[
[\eta_1, \tilde{V}_{\text{Coul}}] = \bar{v}_{2345} \varepsilon_{3_6}^{12} Z^{3b} \eta_4 \eta_5. \tag{61}
\]

In the case when \( \eta_1 = c_1 \) and \( \eta_2 = c_2 \), the operator \( Z^{3b} = 1 \) and \( \varepsilon_{3_6}^{12} = O_{1,2}^{-1} \). In the equation for the GF the term generated by \( [\eta_1, \tilde{V}_{\text{Coul}}] \) can be written as follows

\[
\bar{v}_{2345} \varepsilon_{3_6}^{12} \left[ \langle Z^{3b}(t^+) + i \frac{\delta}{\delta U^{3b}(t^+)} \rangle_U \right. \\
\times \langle T \eta_3^\dagger(t) \eta_4(t) \eta_5^\dagger(t') \rangle_U \right. \\
= \bar{v}_{2345} \varepsilon_{3_6}^{12} \left[ \langle Z^{3b}(t+++) \rangle + i \frac{\delta}{\delta U^{3b}(t++)} \right] \\
\times \left. \langle T \eta_3^\dagger(t^+) \eta_4(t^+) \rangle_U \right. \\
\quad \times \left. \left. G_{\eta_5^\dagger}^{\eta_1}(t, t'|U). \tag{62}
\right. \right.
\]
Here $t^{++}$ and $t^+$ denote the limits $\lim_{t_{1+} \to t_{1+}+0}$ and $\lim_{t_{2+} \to t_{2+}+0}$ respectively. Recall that $[F_0^{\pm\pm}(t', t'|U)^{-1}]_{31'}$ does not depend on the fields $U^{3k}$ and, therefore, $\delta F_0^{\pm\pm}(t', t'|U)/\delta U^{3k}(t')$ can give non-zero contributions only via the mixed GFs $\propto \langle t_c X^1 \rangle$. Therefore, we can write the equation for the GF in the following form

$$G_{11'} = D_0^{11'} P_{11'}^{11'} + D_0^{11'} \varepsilon_{4,3,2}^{1/2} \left[ (Z^{4k}) + i \frac{\delta}{\delta U_{4k}} \right]$$

$$\times \left[ V_{23} + U_{23} \right] G_{33'}$$

$$+ D_0^{11'} \varepsilon_{4,2}^{1/2} \left[ (Z^{4k}) + i \frac{\delta}{\delta U_{4k}} \right]$$

$$\times \bar{v}_{[23]45} \left[ -G_{43}(t_3^+, t_3) + i \frac{\delta}{\delta U_{34}(t_3^+)} \right] G_{55'},$$

where for brevity we write the time argument only in those places where a confusion may arise. The mixing and hopping are denoted by $V$ following the definitions in I. We see that there is an essential difference with the standard WCPT: here we have to calculate the functional derivatives twice, while in WCPT only second square bracket is present. Now let us, in order to give the reader a feeling of the SCPT, make the first iterations and give both the analytical and graphical expressions for the corrections to the GF. In zero order of SCPT $G_{11'} = G_{11'}^0 = D_0^{11'} P_{11'}^{11'}$. Let us now insert $G_{11'} = G_{11'}^0$ into the right-hand side. We have the terms where $\delta/\delta U = 0$,

$$\delta G_{11'}^{1(1)} = D_0^{11'} \varepsilon_{4,2}^{1/2} (Z^{4k}) [V_{23} + U_{23}] G_{33'}^0$$

$$- D_0^{11'} \varepsilon_{4,2}^{1/2} \left[ (Z^{4k}) \bar{v}_{[23]45} G_{43}(t_3^+, t_3) G_{55'}^0 \right].$$

(64)

Since $\varepsilon_{4,2}^{1/2} (Z^{4k}) = P^{1/2}$ and $G = DP$, we have simply

$$\delta G_{11'}^{1(1)} = G_{12}^{0} [V_{23} + U_{23}] G_{33'}^0$$

$$- G_{12}^0 P^{1/2} \bar{v}_{[23]45} G_{43}(t_3^+, t_3) G_{55'}^0.$$

(65)

We denote the pseudolocator $D$ by a solid line with arrow in the Feynman graphs, the end-factor $P$ with an open circle, for the mixing-hopping plus external field, $V + U$, a wavy line is used and for the Coulomb interaction we use a dashed line. Below, we will also need a notation for the Bose-like correlation function $K_{12}^{2k}(t, t') = \delta (Z^{4k}(t)) / \delta U_{23}(t')$: we will use the curly line for it. The graphs Fig. 1, and Fig. 3 correspond to the analytical expressions in Eq. (64). Since $\delta G_{12}^0 / \delta U_{34} = 0$ and this derivative removes one of the interactions $[V_{23} + U_{23}]$ in any expression, in order to obtain the other graphs of first order with respect to Coulomb interaction, we have to insert $G_{51'}$, $\Rightarrow \delta G_{51'} = G_{52}^0 [V_{23} + U_{23}] G_{33'}^0$, into the generating equation. Then, the term with the derivative $\delta/\delta U_{34}$ produces the exchange graph (see Fig. 3):

$$G_{12}^0 \bar{v}_{[23]45} G_{53}^0 G_{51'}^0.$$

(66)

Next, we find four terms generated by the derivative $\delta/\delta U_{4k}$:

$$D_0^{11'} \varepsilon_{4,2}^{1/2} \bar{v}_{[23]45} D_0^{46} (t_3^+, t_6) G_{73}^0 (t_7, t_3) G_{51'}^0$$

$$- D_0^{11'} \varepsilon_{4,2}^{1/2} \bar{v}_{[23]45} D_0^{46} K_{6,4} G_{51'}^0$$

$$+ D_0^{11'} \varepsilon_{4,2}^{1/2} \bar{v}_{[23]45} G_{43}^0 (t_3^+, t_3) D_0^{56} G_{67}^0$$

$$- D_0^{11'} \varepsilon_{4,2}^{1/2} \bar{v}_{[23]45} G_{43}^0 (t_3^+, t_3) D_0^{56} K_{6,6}.$$

(67)

(68)

(69)

(70)

The corresponding graphs are shown in the Figures 3, 4, 5 and 6 respectively. Continuing these iterations we find that there are a subsequence given by the graphs in the Figures 3, 4, 5, and 6, which exactly have the structure of the WCPT: the only difference is that instead of Fermion GFs, $F$, in WCPT here we are dealing with the GFs, $G$. Obviously, each one of these GFs, $G$, can be dressed with hopping and mixing, as shown in Fig. 3, if the corresponding transition is in the energy region where these interactions are not equal to zero (see next sections).

Then, these GFs describe delocalized transitions, or, in other words, Hubbard type of bands. The graphs 7, 8, 9 and 10 do not appear in WCPT for the single-electron GFs and describe contributions from kinematic interactions. Let us now return to the definition, Eq. (64), of the Coulomb matrix elements, $\bar{v}_{[23]45}$, and consider, for example,
Therefore, the potential functions take into account some of the features of SCE. The form of the exchange-correlation potential is given in the introduction was to build a bridge between the standard DFT-LDA calculations and SCPT and to find an extension of LDA which is reasonably simple and central result of the present paper. One of our targets was to build a bridge between those abnormal features of some compounds which are different from the normal Fermi liquid have to be described constant, renormalizing the hopping, Coulomb and mixing interactions. One can expect from this comparison that the equation for the GF in ARF we have to neglect in the first bracket of the Eq.(63) destroys the one-to-one correspondence between the WCPT and SCPT in the ARF series. Thus, in order to obtain the graph 4. In the case when one of the indices, in Eq.(67), say, 5, describes a single -electron, there are no additional factors, \( f^{c^\prime} \). If the index 5 correspond to an \( f \)-electron, then there is a factor \( f^{c^\prime} \). Such factors are automatically provided by the matrix elements \( \bar{v}_{12345} \), Eq.(10), for all inner lines, but not for the external ends. Therefore, if we multiply these type of graphs by the external factors, say, for \( c \), and use the expansion of the Fermi operator in terms of the Hubbard operators, we find that

\[
\bar{v}_{12345} \rightarrow \bar{v}_{12345} \sum_{c^\prime} \langle Z^{c^\prime}(t^{++}) \rangle = \bar{v}_{12345} P^{12}.
\]

This condition removes not only the kinematic interactions, but also any of the graphs containing the correlation functions \( K \) (see the figures 3 and 9). It is worth to note that some of these correlators describe spin waves in the magnetic ordered media, therefore, this type of scattering of carriers is beyond the ARF. In spirit the ARF corresponds to the Hubbard-I approximation (in our definition).

This remarkable similarity can be achieved in the level of equations of motion for the GFs. Although this equation is approximate it is still a functional equation, therefore, the similarity holds in any orders of the PT, which can be generated by iterations of these equations. Therefore, the analogue of the RPA in WCPT can be constructed too. This is obvious from the graphs in the figures 11 and 12 and further graphs containing an increasing number of loops. In matrix notation the definition of this approximation arises from the “reduced” differentiation of the GF. Namely, the higher correlation functions arising in the equation of motion are expressed in terms of functional derivatives of the GFs with respect to the bosonic fields which are needed to reproduce these higher order GFs. Thus, we will call the described approximation the ”approximation of renormalized Fermions”. The factor \( P \), is specific for each transition constant, renormalizing the hopping, Coulomb and mixing interactions. One can expect from this comparison that those abnormal features of some compounds which are different from the normal Fermi liquid have to be described by some of the remaining graphs which are not included into the set defined above as ARF. The analogy can be continued, for example, one can introduce the self energy in SCPT within the ARF in the form

\[
\Sigma_{SCPT}^{\text{SCPT}} = \bar{v}_P (\eta^\dagger \eta) + i \frac{\delta}{\delta U} G^{-1},
\]

which is in complete analogue to the standard definition used in the WCPT,

\[
\Sigma_{W\text{CPT}}^{\text{WCPT}} = \bar{v}(\rho) + i \frac{\delta}{\delta U} F^{-1}.
\]

Thus, we have established a one-to-one correspondence between the perturbation theory for single-electron GFs, \( F \), (weak-coupling expansion) and a sub-series in the perturbation theory for the many-electron GFs, \( G \). This is the central result of the present paper. One of our targets formulated in the introduction was to build a bridge between the standard DFT-LDA calculations and SCPT and to find an extension of LDA which is reasonably simple and takes into account some of the features of SCE. The form of the exchange-correlation potential \( v_{h.c.g.}^{\text{F}} \) which is used in DFT-LDA is derived from the theory of the homogeneous electron gas, i.e. for the case of fully delocalized electrons. Therefore, the potential \( v_{\text{DFT}}^{\text{DFT}} \), should be the solution to the Sham equation:

\[
0 = \sum_{\omega} e^{i \omega t^\dagger} \{ P_{12}^{\text{DFT}} (i \omega) [\Sigma_{23}(i \omega) - v_{23}^{\text{DFT}} (i \omega)] F_{31} (i \omega) \},
\]

is expected to have an analytical form close to \( v_{h.c.g.}^{\text{F}} \), only for the delocalized Bloch electrons. The connection between the matrix elements \( \Sigma_{25}(i \omega) \) and the coefficients of expansion \( \Sigma_{34}(i \omega) \) is given by the relation

\[
\Sigma_{25}(i \omega) = \int dx dx’ \phi_2(x_1) \Sigma(x, x’, i \omega) \phi_2^{\ast}(x_2) = 0_{25} \Sigma_{34}(i \omega) O_{45},
\]
In turn, this means that the one-to-one correspondence, equations 14 and 15, found between the WCPT and SCPT series of graphs can be constructively used for the delocalized transitions. The recipe follows from comparison of these two equations: the following replacements should be made in the expression for the self-energy: $F \rightarrow \langle \eta \eta \rangle$ and the matrix element of Coulomb interaction $v \rightarrow \delta P$. Besides, the charge density should be rewritten in the form, where each $f$-operator is represented in terms of $X$-operators: $f_{\sigma} = f^{a}_{\sigma} X^{a}$. As follows from I, and will be shown in details in III, the matrix elements of mixing interaction and overlap matrices are also renormalized by the spectral weights. Let us now compare the equations for the dielectric permeability within WCPT, Eq.(14), and SCPT, On one hand, according to our comparison of graphs, Eq.(64)-(71), and the more general observation, Eq.(72)-(74), in order to transform a graph of WCPT into the one of SCPT we have to replace each bare $f$-GF as follows

$$F^{(0)}_{\nu} = (\omega - \varepsilon^{f}_{0})^{-1} \sum_{a} \frac{|f_{\nu,a}|^{2} P^{a}}{i\omega - \Delta^{a}_{1}}.$$  

(77)

On the other hand, the low-energy transitions does almost not form bands at all. Let us write down the elementary loop (the graph beyond exchange) and separate the lower transitions in it. Each index in the loop

$$\Pi^{(0)}_{12,34}(i\Omega) = T \sum_{i\omega} F_{12}(i\omega) F_{34}(i\omega + i\Omega)$$  

(78)

can take the values $1 = c_{1}, c_{2}, f_{1}, f_{2}$, i.e. the index of a conduction electron, $j_{1}L_{1}$, or one of values for an $f$-electron, $j_{1}L_{1}^{e}$ or $j_{1}L_{1}^{f}$, where $e$ denotes an empty (delocalized) and $f$ stands for a filled (localized) orbitals. If we neglect, for a first step, the contributions from the Coulomb matrix elements with an odd number of $f$-operators, then the lower pole contributes only in the loops, which contain one GF of the $ff$-type, $F_{1,2}$ or $F_{3,4}$. All other loops are standard ones with the only difference that the standard $f$-GFs, $F^{(0)}_{1,2}$, when the $f$-electrons are treated as valent, however they acquire the factor $\sqrt{|(\varepsilon^{f}_{\nu} |^{2} P^{f}}$ where the sum is taken over the upper transitions $a_{2}$, and $\varepsilon^{f}_{0}$ should be replaced by $\Delta^{a}$. Since in the loop

$$\Pi^{(0)}_{12,34}(i\Omega) = T \sum_{i\omega} F_{12}(i\omega) F_{34}(i\omega + i\Omega)$$  

(79)

$$f(\Delta_{a})$$ is always equal to 1 and the Fermi function $f(\varepsilon^{f}_{k\lambda} - \mu) = 0$ only if $\varepsilon^{f}_{k\lambda} > \mu$ , the loops $\Pi^{(0)}_{12,34}(i\Omega)$ have large denominators in the region where the numerator is not equal to zero and, therefore, they are small compared to $\Pi^{(0)}_{12,34}(i\Omega)$. Here, the coefficients $B$ transform the GFs from the orbital representation to the bands $k\lambda$. Thus, it is expected, the main contribution to the screening comes from the conduction electrons including the delocalized upper transitions. Within this approximation the formulas: Eq.(15) for the dielectric permeability $\varepsilon^{-1}$, Eq.(17) for the self-energy $\Sigma^{RPA}$ remains valid, however, with the replacement of the full GF by only the upper-pole part. There are, of course, also contributions from the electrostatic interactions between electrons of different sites, which are treated in a standard way with the difference that each transition enters with its spectral weight.

Let us turn now to the Galitskii-Migdal expression Eq.(13) for the total energy. In the last term of Eq.(13) we have a summation over the transitions. For the lower transitions $O_{j_{1,j_{2}} = \delta_{j_{1},j_{2}}, t_{j_{1},j_{2}} = \delta_{j_{1},j_{2}}^{v} \delta_{j_{1},j_{2}}^{f}}$ and the local terms give a contribution to the energy from the core-like levels. The remaining expression, within the ARF, coincides with the contribution to the energy from delocalized electrons within the WCPT if we make the replacement in the $f$-GFs discussed above. Exactly the same arguments can be applied to the Sham equation, Eq.(17), connecting the many-body GF and the self-energy with the DFT GF and the exchange-correlation potential. Therefore, we can conclude that the analytical form of the exchange-correlation potential used for the description of delocalized electrons can be applied also to the case of correlated electrons if we will use the expression for the charge density Eq.(15) in the form (100) (the derivation is given in next section). Note that in the limit when the lower spectral weight for the localized electrons $P = 1$ and $\Delta_{a} \rightarrow \infty$ we are back to the standard model for the lanthanides (see the next section), since in this case we have $n$ $f$-electrons localized and the upper transitions do not contribute to the energy. Then, the possibility to describe photo-electron spectroscopy disappear. When $P < 1$, we have to solve a system of equations for the spectral weights additionally to a standard DFT calculation and bring these two calculations to self-consistency. The remaining important question, the magnitudes of $\Delta_{1}$ and $\Delta_{2}$ will be discussed in last section.

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3We can do it since even differential overlap between localized $f$-orbitals and delocalized $c$-ones is negligible
Since only a part of the transitions is delocalizing, some difference arises between electrons and quasi Fermionic excitations, which we call renormalized Fermions. First, the numbers of Fermions and renormalized Fermions are different, since the latter is determined by the number of Fermi-like intra-atomic transitions, involved in the physics under consideration. Second, the WCPT generates the graphs describing all intra-core and f-f interactions, relating to the same ion, while they are already taken into account via the algebraic construction of the many-electron state in the GFs, G. The intra-atomic Coulomb interactions are included into the WCPT theory separately; as will be seen later, in SCPT the transitions, describing deep intra-ionic transitions are naturally separated by a big energy gap from the delocalized electrons and actually the discussed mapping involves only the delocalized states, providing, (if necessary) a description of the many-electron structure of the ion including the Hund rules. Third In order to make the two series, WCPT and SCPT, fully analogous in the Coulomb interaction, Eq. (60), and to derive the ARF, we had to treat all terms in the way as if they belonged to different sites. Therefore, we had to add the graphs, which treat the correction to the terms in Eq. (60) with a few f-operators belonging to the same site, and subtract those, which within the ARF, are treated incorrectly. This difference should be included in the error of the ARF. Therefore, the accuracy of this approximation (or an applicability to the physics in question) is determined not only by those graphs which describe the different manifestations of the kinematic interactions, but also by the difference between the correlated and decoupled single-ion terms in the ARF. In Appendix A, we have separated all Coulomb terms into classes containing different number of f(d)-operators (or core-operators): the terms belonging to the class 0 do not contain them at all, the ones belonging to the class 1 contain one f-operator etc. Due to the large number of terms this consideration is quite lengthy. The terms generated by Coulomb interaction in the equations of motion for Green functions operators are given in Appendix A.

In order to estimate the error, due to this difference between the correlated and decoupled single ion terms, we have to take all the graphs which contain some of the sites, or all of them, coinciding and subtract the graphs with the same value of the matrix element of Coulomb interaction but with the analytical expression for the set of the GFs corresponding to certain choice of links between sites. The sites are defined as linked if they belong to the same value of the matrix element of Coulomb interaction but with the analytical expression for the set of the GFs, corresponding to certain choice of links between sites. Therefore, we had to add the graphs, which treat the correction to the terms in Eq. (60) with a few f-operators belonging to the same site, and subtract those, which within the ARF, are treated incorrectly. This difference should be included in the error of the ARF. Therefore, the accuracy of this approximation (or an applicability to the physics in question) is determined not only by those graphs which describe the different manifestations of the kinematic interactions, but also by the difference between the correlated and decoupled single-ion terms in the ARF. In Appendix A, we have separated all Coulomb terms into classes containing different number of f(d)-operators (or core-operators): the terms belonging to the class 0 do not contain them at all, the ones belonging to the class 1 contain one f-operator etc. Due to the large number of terms this consideration is quite lengthy. The terms generated by Coulomb interaction in the equations of motion for Green functions operators are given in Appendix A.

In order to estimate the error, due to this difference between the correlated and decoupled single ion terms, we have to take all the graphs which contain some of the sites, or all of them, coinciding and subtract the graphs with the same value of the matrix element of Coulomb interaction but with the analytical expression for the set of the GFs corresponding to certain choice of links between sites. The sites are defined as linked if they belong to the same site. These different choices are considered in Appendix A. The interaction of the density-density type is expected to give the main contribution, therefore, let us consider the graph b as an example. It takes into account the Hartree contributions from the terms of the Coulomb Hamiltonian: 

\[ V_1^C = \tilde{v}_{j_2j_3j_4j_5}X_{j_2j_3}^{a_2}X_{j_4j_5}^{a_3}, \]

\[ V_2^C = \tilde{v}_{j_2j_3j_4j_5}X_{j_2j_3}^{a_2}X_{j_4j_5}^{a_3} \]

whereas the term which has been added for inclusion into the ARF and, therefore, subtracted, is 

\[ \tilde{v}_{j_2j_3j_4j_5}X_{j_2j_3}^{a_2}X_{j_4j_5}^{a_3}, \]

The difference is

\[ \tilde{v}_{j_2j_3j_4j_5}X_{j_2j_3}^{a_2}X_{j_4j_5}^{a_3} \]

It is convenient to use the equality

\[ \kappa_\xi^{\alpha_3a_4} \varepsilon_\xi^{\alpha_b} = \varepsilon_\xi^{\alpha_3a_4} \kappa_\xi^{\alpha_b}, \]

which follows from the commutation relations between Hubbard operators. Then, the difference between the terms is proportional to

\[ (\langle Z_\xi^j \rangle \delta_\alpha_4 b + \kappa_\xi^{\alpha_4a_3} \varepsilon_\xi^{\alpha_3a_4}) \]

for diagonal \( \xi = [\Gamma, \Gamma] \) this is \( (1 - P_{\alpha_4}) \). Now we will use an information about the spectral weights which is considered in details in the next sections. Both, localized and delocalized f-orbitals have upper (\( \Delta_4 \sim \Delta_1 \)) and lower (\( \Delta_2 \sim \Delta_2 \)) transitions. For localized orbitals and for lower transitions \( \tilde{a}_2 \) or \( \tilde{b} \) in Eq. (62) the expectation values,
\[\langle X_\alpha^a X_\beta^b \rangle \text{, are small } (\ll 1) \text{ due to the suppressed hopping and mixing in the region of energies at energies } \omega \sim \Delta_n \text{ and big energy gap } \varepsilon_F - \Delta_n ; \text{ the latter suppresses admixture across the gap. For the upper transitions the localized orbitals themselves have in this region of energies small spectral weight and again } \langle X_\alpha^a X_\beta^b \rangle \ll 1. \text{ The weight } P^a \text{ is close to unity for the delocalized orbitals near the upper transitions } (\Delta_2), \text{ therefore, the small constant decreasing the difference in Eq. (23) is } \alpha = (1 - P^a). \]

It is also worth to discuss a possible confusion: it may seem that these speculations are wrong just for the simple reason that the equation for the GF in the WCPT is \textit{exact} while both representations (single-electron Fermionic and many-electron) are equivalent; therefore, WCPT must generate some graphs which should not appear in the SCPT for an approximate equation for the GF in SCPT. Indeed, all this consideration might be performed within the WCPT, however, in this case one has to consider the theory, not for the single-electron GFs, \( F \), in WCPT but, for the many-electron ones, \( G_F(x_1, x_2, x_3, ..., x_n) \), (here \( x_i = (r_i, t_i) \) ) which correspond to the functions \( G_X \). The functions \( G_F(x_1, x_2, x_3, ..., x_n; R_f) \) describe the relative motion of all \( n \) electrons in an ion and, therefore, contain much more information than we actually need. This means that to find them require much more effort than for the simplified functions \( G_X \), which are constructed on many-electron operators, \( X(t) \), belonging to the same time, \( t \). Of course, the same argument shows the insufficiency of the approach discussed in the cases when a knowledge of the dynamics of each electron is essential. This situation arises when the magnitude of the perturbation is so large, that the complexes are destroyed completely. In Appendix \[ \text{we consider a simple example, illustrating the difference in the descriptions already in the level of the ARF. Now we shall consider how the standard model for the lanthanides,} \]

widely used in \textit{ab initio} methods, arises in our approach.

III. STANDARD MODEL FOR THE LANTHANIDES AND ITS EXTENSION

It is instructive to consider the limiting case corresponding to the so-called \textit{standard model} for the rare earths first, where the \( f \)-electrons are assumed to be completely localized and atomic like. We will show that this model sometimes needs to be modified, in order to explain all experimental data of the lanthanides. Let us first have a look at the structure of the zero Fermion GF in the atomic limit, which is given by

\[
F^{(at)}(i\omega) \equiv \langle T f_{\nu} f_{\nu}^\dagger \rangle_{i\omega} = \sum_a \frac{|f_a|^2 P^a}{i\omega - \Delta_a} \\
\equiv \sum_{\{\Gamma_n\}} \left| \langle \Gamma_n | f_{\nu} | \Gamma_{n+1} \rangle \right|^2 \frac{(N_{\Gamma_n} + N_{\Gamma_{n+1}})}{i\omega - (E_{\Gamma_{n+1}} - E_{\Gamma_n})}.
\]

The differences of the energies of the ion states \( E_{\Gamma_{n+1}} - E_{\Gamma_n} \sim E_{\Gamma_n} - E_{\Gamma_{n-1}} \sim U \), i.e. of the order of value of Hubbard \( U \); here \( n \) is the number of localized electrons of the element in question in a given compound. Due to the large value of \( U \) the transition \( E_{\Gamma_n} - E_{\Gamma_{n-1}} \equiv \Delta_{\Gamma_{n-1}\Gamma_n} \) in many cases (particularly, in rare earths) is much below the bottom of the valence bands, while the transition \( E_{\Gamma_{n+1}} - E_{\Gamma_n} \equiv \Delta_{\Gamma_n\Gamma_{n+1}} \) is above the Fermi level (as seen from spectroscopic data, in many rare earths it is not very high above \( \varepsilon_F \)). The strength of the hopping and mixing depend on the energy of the states involved since the width of the inter-atomic barrier for electron tunneling is increasing with a decrease of the energy and also, the intra-atomic states of an isolated ion belonging to different energies are orthogonal to each other; for the deep states of a non-isolated atoms this picture is changed only by a small amount. On one hand, as discussed earlier (see Fig.5.6 in Ref.\[ \]), the mixing interaction and hopping gradually, but quite fast, are switching off when, say, the \( f \)- or \( d \)-level moves deeper to the energy region below the bottom of a band. In our language this corresponds to the lower transitions, \( \Delta_{\Gamma_{n-1}\Gamma_n} \). Therefore, only the upper transitions, which are in the proximity of the Fermi level, can participate in the formation of bands. However, if the upper transition is much higher than \( \varepsilon_F \), the bands formed are not occupied and do not contribute to the cohesive energy. From the physical point of view this picture is fully analogous to the standard model: in both cases the localized, occupied, \( f \)-bands contribute to the total energy as core states while the contribution to the cohesive energy in both cases is absent.

The arguments given in the simple example in Appendix \[ \text{can be easily extended to the general case of } n \text{ orbitals.} \]

Let us show how this separation (or, in another language, \textit{"orbital polarization"}) arises. The immediate objection often arising is that from the point of view of simple models of strongly correlated electrons, say, Hubbard-like models, the

\[ \text{It should be noted that this statement is representation dependent and relates to the methods where the intra-atomic wave functions in the basis set are taken as atomic-like.} \]
switching off of mixing and hopping seems strange. Indeed, the transformation of the Hamiltonian from the Fermion
representation to the representation of Hubbard interactions is exact,

\[ \mathcal{H}_{\text{Hubb}} = \sum_{\langle ij \rangle} (e^0_{ij} \delta_{ij} \delta_{\lambda\nu} + t^{ij}_{\lambda\nu}) f^\dagger_{i\lambda} f_{j\nu} + \sum_{i\sigma} U \hat{n}_{i\lambda} \hat{n}_{i\sigma} \]  

(86)

\[ = \sum_{i\sigma} e^0_{i\lambda} X_i^{[\lambda,\lambda]} + \sum_{i,\lambda \neq \nu} (e^0_{\lambda} + e^0_{\nu} + U) X_i^{[\lambda,\nu,\lambda,\nu]} + \ldots \]

\[ + \sum_{\langle ij \rangle \lambda \mu} \langle \lambda_1 | f^\dagger_{i\lambda}|0\rangle X_i^{[\lambda_1,\lambda]} \]

\[ + \langle \lambda_1 | f^\dagger_{i\lambda}|0\rangle X_i^{[\lambda_1,\mu,\mu]} + \ldots \]

\[ \times \left[ \langle \lambda | f^\dagger_{i\lambda}|\lambda_2\rangle X_i^{[\lambda,\lambda_2]} + \langle \lambda | f^\dagger_{i\lambda}|\lambda_2\mu\rangle X_i^{[\lambda,\lambda_2,\mu]} + \ldots \right], \]  

(87)

therefore, if one writes the same magnitude of hopping for all orbitals, \( t^{ij}_{\lambda\nu} = t_{ij} \), its magnitude for the lower transitions coincides with the one for the upper transitions. Here we have written a truncated single-site Coulomb interaction in order to simplify the discussion; the Greek indices denote the orbitals: \( \lambda = (i, m, \sigma) \), the vacuum state \( |0\rangle \) includes all filled shells of ion, \( |\lambda\rangle = f^\dagger_{i\lambda}|0\rangle \), \( |\lambda\mu\rangle = f^\dagger_{i\lambda} f^\dagger_{i\mu}|0\rangle \), etc., and the orbital \( \lambda \) belongs to an open shell. However, this is an oversimplification which makes the physics different from what happens in reality the hopping is always orbital dependent. Let us denote the occupied orbitals of the shell by \( \nu_f \), and unoccupied ones by \( \nu_e \). In lowest order one expects that the Hubbard sub bands will be generated by the poles of the Fermionic GF. Indeed, the "band structure" in the Hubbard-I approximation for the model \( t^{ij}_{\lambda\nu} = \delta^{ij} t^{i}_{ij} \) is given by the equation:

\[ F_{\nu}^{-1}(\omega) = \left[ \sum_{a} \frac{|f_{\nu a}|^2 P_{\nu a}}{\omega - \delta_{\nu a} + i\Gamma_{\nu a}} \right]^{-1} - t^{\nu}_{k} = 0. \]  

(88)

However, as discussed above, if the orbital \( \nu_f \) is deep in the potential well, the hopping \( t^{ij}_{\nu_f} \) becomes so small (exponentially) that the bandwidth becomes of the order of the width of the transition, \( \Gamma_{\nu} \) (the width is due to interaction with phonons, electro-magnetic fluctuations etc.). In this region of parameters the coherence is destroyed and bands are not formed. Besides, the bare hopping entering this equation, actually, does not determine the real band structure: the equation for it contains the self-energy which also should be found self-consistently (in both, WCPT and SCPT); the hopping itself in the Hubbard representation is treated as an interaction and is dressed either with the vertex corrections within field-theory methods or, via changes of the wave functions within \( \text{ab initio} \) band structure methods. Second, as follows from the observation that any element shows a valence which is either integer, or, for the compounds with intermediate valence, between to nearest integers in a given surrounding and pressure, only three groups of the transitions

\[ \Delta_{\bar{a}_1} = \Delta_{\bar{a}}^{(n,n-1)} = E^{\Gamma_n} - E_{\Gamma_{n-1}} \]

\[ \Delta_{\bar{a}_2} = \Delta_{\bar{a}}^{(n+1,n)} = E^{\Gamma_{n+1}} - E_{\Gamma_n} \]

\[ \Delta_{\bar{a}_3} = \Delta_{\bar{a}}^{(n+1,n)} = E^{\Gamma_{n+2}} - E_{\Gamma_{n+1}}, \]  

(89)

can contribute to the Fermionic GF. Here \( n \) is the number of localized electrons in the ion. In order to simplify the discussion we take \( |\Gamma_n\rangle \) in the simple form: \( |\Gamma_n\rangle = f^\dagger_{i1} f^\dagger_{i2} \ldots f^\dagger_{in}|0\rangle \), put \( \Delta_{\bar{a}_i} = \Delta_n \), \( i = 1, 2, 3 \) and omit the widths of the levels \( \Gamma_{\bar{a}_i} \). Then the matrix elements \( |f_{\nu a}^{ij}|^2 = \langle 0|f_{f_{\nu a}^{ij}} f_{\nu a}^{ij}|f_{f_{\nu a}^{ij}} f_{\nu a}^{ij} ... f_{f_{\nu a}^{ij}} f_{\nu a}^{ij} |0\rangle^2 = 1 \) and are equal to zero if the orbital \( \nu \) is not present in the state \( |\Gamma_n\rangle \) and the equations for the spectrum become

\[ F_{\nu_f}^{-1} = \left[ F^{0}_{\nu_f} \right]^{-1} - t^{\nu_f}_{k} \]

\[ = \frac{P_{\nu a_{1}}^{\nu a_{1}}}{\omega - \Delta_n} + \frac{P_{\nu a_{2}}^{\nu a_{2}}}{\omega - \Delta_2} + \frac{P_{\nu a_{3}}^{\nu a_{3}}}{\omega - \Delta_3} - t^{\nu}_{k} = 0; \]  

(90)

\[ F_{\nu_e}^{-1} = \left[ F^{0}_{\nu_e} \right]^{-1} - t^{\nu_e}_{k} \]

\[ = \frac{P_{\nu a_{1}}^{\nu a_{1}}}{\omega - \Delta_1} + \frac{P_{\nu a_{2}}^{\nu a_{2}}}{\omega - \Delta_2} + \frac{P_{\nu a_{3}}^{\nu a_{3}}}{\omega - \Delta_3} - t^{\nu}_{k} = 0, \]  

(91)

where
\[
\sum_{\alpha_i} |f_{\nu_0}^{\alpha_i}|^2 P_{\nu_0}^{\alpha_i} = P_{\nu_0}, \quad \sum_{\alpha_i} |f_{\nu_0}^{\alpha_i}|^2 P_{\nu_c}^{\alpha_i} = P_{\nu_c}^{\alpha_i}.
\]

Let us consider the combinations of the population numbers \(P^\alpha = P^\alpha(\Gamma, \Gamma')\), which are the spectral weights for the non-perturbed Fermionic GFs. For simplicity we also take the sum rule for the population numbers in the form \(\sum_{\Gamma} N_\Gamma = 1\) (recall that this sum rule is representation dependent; it follows from the commutation relation \(\{f_{\nu \nu'}, f_{\nu \nu'}^\dagger\} = 1\), but this is valid only for the orthogonal basis set of wave functions; in the case of non-orthogonal set \(\{f_{\nu \nu'}, f_{\nu \nu'}^\dagger\} = O^{-1}_{\nu \nu'}\) and the sum rule is also different). According to our assumption the ion has \(n\) electrons localized, i.e., the states \(\sum C^{(l)}_{\nu_1, \nu_2, \ldots, \nu_n, f_{\nu_1}^\dagger, f_{\nu_2}^\dagger, \ldots, f_{\nu_n}^\dagger} |0\rangle = |\Gamma_n^{(l)}\rangle\) are filled in the non-interacting ion. If the interactions which remove the degeneracy of these states are absent (not taken into account, or the temperature is higher than the corresponding splitting), then, there is no physical reason for the population numbers of these states to be different. Let us calculate the population numbers of the states involved for one chosen orbital and then use the symmetry between the orbitals. Let us choose the orbital \(\nu = 1\). Then any of the transitions \(f_{1}|1, \nu_1, \nu_2 \ldots \nu_{n-1}\rangle \rightarrow |\nu_1, \nu_2 \ldots \nu_{n-1}\rangle\) for \(\nu_i\) from the set \(\nu = 2, 3, \ldots, N\) gives a non-zero matrix element \(|f_{\nu_0}^{\alpha_i}|^2\); therefore

\[
N_{\Gamma_1^{(1)}}^0 = \binom{N}{n}^{-1} \equiv C_n^m,
\]

and all other population numbers are zero. Then

\[
P_{\nu_0}^{\alpha_1} = \sum_{\alpha_1} |f_{\nu_0}^{\alpha_1}|^2 \sum_{\Gamma} \sum_{\Gamma'} C_{\nu_1, \nu_2, \ldots, \nu_n, f_{\nu_1}^\dagger, f_{\nu_2}^\dagger, \ldots, f_{\nu_n}^\dagger} N_{\Gamma_1^{(1)}}^0 \equiv N_{\Gamma_1^{(1)}}^0 + N_{\Gamma_n}^0 = N_{\Gamma_1^{(1)}}.
\]

and

\[
P_{\nu_0}^{\alpha_1} = \sum_{\alpha_1} |f_{\nu_0}^{\alpha_1}|^2 \sum_{\Gamma} \sum_{\Gamma'} C_{\nu_1, \nu_2, \ldots, \nu_n, f_{\nu_1}^\dagger, f_{\nu_2}^\dagger, \ldots, f_{\nu_n}^\dagger} N_{\Gamma_1^{(1)}} + N_{\Gamma_n} = N_{\Gamma_1^{(1)}} + N_{\Gamma_n}.
\]

Therefore, the zero Fermion GF for the particular orbital \(\nu_0\) is

\[
F_{\nu_0, \nu_0} = \frac{C_{N-1}^m N_{\Gamma_n}}{\omega - \Delta_1} + \frac{C_{N-1}^m N_{\Gamma_n}}{\omega - \Delta_2} = \frac{C_{N-1}^m C_N}{\omega - \Delta_1} + \frac{C_{N-1}^m C_N}{\omega - \Delta_2}
\]

\[
= \frac{n/N}{\omega - \Delta_1} + \frac{(N-n)/N}{\omega - \Delta_2}.
\]

The total spectral weight is equal to one as it should be. However, at \(\omega = \Delta_1\) we have the weight \(n/N < 1\), while the weight of the low-energy transition from all \(N\) orbitals is \(n\), as it is expected within a single-electron picture. Thus, within the non-polarized picture one can expect from Eq. (96) that the bandwidth of the lower Hubbard sub bands will be proportional to \(n/N\) and the upper one to \((N-n)/N\). 5 This paramagnetic picture is, however, too rough. First, this speculation does not reflect the fact, established in the \(ab\) \(initio\) calculations, that if the energy \(\Delta_n\) is below the bottom of the lowest conduction band, any matrix element of hopping or mixing, calculated within self-consistent scheme becomes negligible. Second, the degeneracy is certainly overestimated: the first Hund rule is caused by the intra-atomic exchange integrals, but the splitting between different orbitals may be a few such integrals (say, the transitions between three-electron states and two electron ones cover the range from \(2U - 2J\) to \(2U - 9J\), where \(J\) is exchange integral); the next-order Coulomb interactions, which are responsible for the second Hund rule, are also much greater than room temperature; at last, the spin-orbit coupling, for example, in rare earths provides a splitting of eV-order, between the multiplets. Thus, if the atomic-like Hund rules are not fully destroyed we find in a zero approximation that only one of the population numbers \(N_{\Gamma_1^{(1)}} \approx 1\), and, therefore, due to the sum rule, \(\sum_{\Gamma} N_{\Gamma}^0 = 1\), all remaining \(N_{\Gamma_1} = 0\). The GFs

\[
G_{\alpha_1}^{(0)}(\omega) = \frac{P_{\nu_0}^{\alpha_1}}{\omega - \Delta_{\alpha_1}} \approx \frac{1}{\omega - \Delta_{\alpha_1}},
\]

\[
G_{\alpha_2}^{(0)}(\omega) = \frac{P_{\nu_0}^{\alpha_2}}{\omega - \Delta_{\alpha_2}} \approx \frac{1}{\omega - \Delta_{\alpha_2}},
\]

5Within the diagrammatic field-theory methods this problem in the case of degenerate states is not solved yet and we postpone this for a future work.
and the Fermion GF for the filled orbitals is

\[ F_{v_0} \approx \frac{1}{\omega - \Delta_{a_1}}, \]  

(98)
i.e. we are dealing with the situation, considered in the example in Appendix $\mathbb{B}$. Thus, let us switch on the hopping and mixing. We have to distinguish the Hubbard sub bands originating from empty and filled orbitals since hopping for them are different.

In the case of empty orbitals the hopping $t_{v_\nu} \neq 0$ since they have energies above Fermi energy, where the potential barrier between atoms either is absent or is small. However, as we have seen in the previous section, the dispersion of the lower Hubbard sub band is negligible due to the small weight of these orbitals in this region of energies. In the case of filled orbitals the dispersion in the lower Hubbard bands is also negligible since $t_{v_\nu}$ is small due to the large width and height of the energetic barriers between atoms; near the upper transition their spectral weight is small. Thus, the only dispersion which is physically important is the dispersion of the empty orbitals near the upper transitions. Above we have shown that the switching of the mixing and hopping leads to the appearance of non-zero spectral weights, above the Fermi level for the filled orbitals and for the empty orbitals in the region of lower transitions. But the dispersion in the latter region is negligible for both type of orbitals. Therefore, the role of delocalized electrons is played by delocalized upper transitions of the empty orbitals and we can use this fact in order to derive some recipe for how to correct the exchange-correlation potential. On the other hand, we can in the general formulas use the approximation $\varepsilon_{\nu} \approx 0$ as well as the overlap matrix with neighbors should be zero. This leads to a disperse-less lower Hubbard band. As we see, Eq. (97) and (98) correspond to the standard model for the lanthanides if the upper transitions will not contribute to the cohesive energy and this situation arises when the energy of the upper transition $\Delta_{a_2} \gg \varepsilon_F$. As known from electron spectroscopy, this is not the case even for rare earths $\mathbb{B}$. However, as we have seen above, if the mixing interaction of the conduction bands with the upper transition is not equal to zero, the spectral weight at both, upper and lower energies, deviates from unity and, therefore, it is desirable to correct the localized model at least in this place. Let us introduce this correction.

The exchange-correlation potential is a function of total charge density. Within the real-space representation of atomic-like wave functions this charge density is given by Eq. (100), where the Fermion GF $\langle T_{a_1}a_1^\dagger \rangle_\omega$ should be represented via the many-electron GFs, $G$. Within the approximation of dispersion-less lower transitions $\Delta_{a_1}$ we can write the structure of the $XX$-GFs as follows:

\[ G_{ja,j'a'}^{(XX)}(\omega) \simeq \delta_{jj'} \delta^{aa'} \delta^{aa_1} \frac{P_{a_1}^{a}}{\omega - \Delta_{a_1}} + \delta^{aa_2} \delta^{aa'} G_{ja_2,j'a_2}^{(XX)}(\omega), \]  

(99)

while all other GFs, $G^{(Xc)}$, $G^{(cc)}$ and $G^{(cX)}$, do not have the lower pole due to the absence of hopping and mixing in this region of energy. Here $a_1$ denote the lower transitions and $a_2$ the upper ones. Inserting this formula into the expression for the charge density, Eq. (100), we find in terms of retarded GFs

\[
\rho(x) = -\frac{1}{2\pi} \int d\omega \frac{1}{e^{\beta(\omega - \mu)} + 1} \\
\times \left\{ \lim_{x' \to x} \left[ \sum_{jL,j' L'} \phi_{jL}(x)\phi_{j' L'}(x') Im F_{jL,j' L'}(\omega + i\delta) \right. \right. \\
+ \left. \left. \sum_{j\nu a,j' L'} \phi_{j\nu}(x)\phi_{j' L'}(x') (f_{\nu})^a Im G_{ja,j' L'}^{(Xc)}(\omega + i\delta) \right] \right. \\
+ \left. \lim_{x' \to x} \left[ \sum_{jL,j' \nu a} \phi_{jL}(x)\phi_{j' \nu a'}^*(x') (f_{\nu})^a (f_{\nu}^\dagger)^{a'} Im G_{ja,j' \nu a}^{(cX)}(\omega + i\delta) \right. \right. \\
+ \left. \left. \sum_{j\nu a,j' \nu' a'} \phi_{j\nu}(x)\phi_{j' \nu' a'}(x') (f_{\nu})^a (f_{\nu}^\dagger)^{a'} Im G_{ja,j' \nu a}^{(cX)}(\omega + i\delta) \right] \right. \\
+ \left. \lim_{x' \to x} \sum_{j\nu a,j' \nu' a'} \phi_{j\nu}(x)\phi_{j' \nu' a'}(x') (f_{\nu})^a P_{a}^{a'} \right\} \\
\times \frac{1}{e^{\beta(\Delta_{a} - \mu)} + 1} \left(f_{\nu}^\dagger \right)^{a'}. \]  

(100)
The last term represents the contribution of the core states into the spectrum of the Fermion-like excitations. This expression differs from the standard one used in ab initio calculations only by the numbers $P^a$, which are present in the last term and all GFs. At zero temperature $P^a$ are determined mainly by the strength of the $c$-$f$-mixing, $f$-$f$-hopping and the proximity of $\Delta_0$ to the Fermi energy. In the last term the factor $P^a/[e^{\beta(\Delta_0-\mu)}+1]$ for the transition $a=[\gamma, \Gamma]$ gives the statistical weight with which the orbitals $\nu_0, \nu'_0$ contribute to the states $[\gamma], [\Gamma]$.

The expression for the total energy has the same ingredients, but the additional integral over coordinates gives the overlap matrixes and and matrix elements of the kinetic energy. Therefore, we find for the total energy

$$E_{\text{tot}} = -\frac{1}{2\pi} \int d\omega \frac{1}{e^{\beta(\omega-\mu)}+1}$$

\begin{align*}
&\times \left\{ [O_{j_1,L_1,j_2,L_2}\omega + t_{j_1,L_1,j_2,L_2}]ImF_{j_2,L_2,j_1,L_1}(\omega + i\delta) \\
&+ [O_{j_1,L_1,j_2,\mu}\omega + t_{j_1,L_1,j_2,\mu}]f_{\mu}^b \delta_{\mu,j} \frac{1}{e^{\beta(\Delta_0-\mu)}+1} \right\} \\
&+ \sum_j [\delta_{\mu_1,\mu_2}\Delta_{\mu_2} + t_{j,\mu_1,j,\mu_2}]f_{\mu_2}^a (f_{\mu_1}^b) \delta_{\mu_1,\mu_2} \frac{1}{e^{\beta(\Delta_0-\mu)}+1}.
\end{align*}

(101)

Here $t$ is kinetic energy.

IV. DISCUSSION AND CONCLUSIONS

The ab initio calculations based on the LDA in DFT has become a quite reliable method for investigating the solid state. The materials with strongly correlated electrons, which forms a quite wide class (high-$T_c$ superconductors, doped Mott insulators, materials with colossal magneto resistance, heavy-Fermion systems and Kondo lattices and, different artificial structures based on small quantum dots) and are used in more and more applications, are traditionally difficult for ab initio calculations. It is well-known that these difficulties often are caused by the localized or quasi-localized electrons originating from open electronic shells of transition elements, lanthanides or actinides. Three methods found for overcoming these difficulties, LDA+$U$, self-interaction correction (SIC), and the complete localization model for lanthanides (where all $f$-electrons are forced to be core states) provide the same physics: they localize some of the electrons, making the potentials for conduction electrons and for localized ones, different. On one hand, since at least LDA+$U$ and SIC use more than one potential, they go beyond the DFT scheme, where only one potential corresponds to a charge density in ground state. On the other hand, there always questions, How to avoid double-counting? What is “Hubbard $U$”? Why is SIC applied to certain orbitals and not to other ones? etc., for which it is difficult to give an answer without considering the full problem (say, in the language of some of perturbation theories) and understanding what is included into LDA. An answer to first question has partly been found by Kotani [7], who has shown that the LDA potential corresponds to a static random phase approximation. This simultaneously gives an answer to the question why the Hartree-Fock calculations give much less accurate results than the ones in LDA: LDA takes into account screening, while the Hartree-Fock method does not. However, this is only a part of the answer since, on the one hand, in modern calculations the exchange-correlation potential is taken from the (parameterized) results of Monte-Carlo simulations for homogeneous electron gas, which certainly, go beyond RPA. On the other hand, these statements and investigations are based on an analysis of either the homogeneous or weakly inhomogeneous electron gas. What can be done in the case of a strongly inhomogeneous electron liquid? The LDA+$U$ and SIC methods are intended for this case and, as was mentioned above, they go beyond the DFT ideology and contains some open questions. As we see, the problem of understanding, in a formal language, what is included into LDA and what should be taken into account additionally in it to describe correlated systems are necessary steps in the development of the theory of solids. In the present work we made an attempt to obtain the physical picture analogous to the one generated by these three methods, but to perform such an analysis on the basis of solid grounds. Here we have used the perturbation theory from the atomic limit developed in a previous paper (ref. [7]) for the case of the generalized multi-orbital Hubbard-Anderson models and extended it for the case of inter-site Coulomb interaction. We have considered the easiest case, when a part of the electrons of the $f$-shell is well localized. The picture, generated by the perturbation theory is the following.

First, under the word ”correlations” we mean that the intra-atomic interactions are strong enough to make it necessary to calculate $\langle \hat{n}\hat{n} \rangle$ beyond the decoupled form $\langle \hat{n} \rangle \langle \hat{n} \rangle$. Here, we use the exact relation $\langle \hat{n}\hat{n} \rangle = \langle \hat{n} \rangle$. This
immediately leads to the formation of a energy gap between the occupied and empty orbitals. Therefore, taking into account local correlations automatically leads to orbital polarization, the picture which is obtained in the methods LDA+U and SIC. The potentials for "upper" and "lower" orbitals differ from each other, roughly speaking, by the Hubbard $U$.

Second, the language of the localized and delocalized orbitals is not completely correct: since the orbitals are coupled by interactions to complexes, described by many-electron wave functions, the role of the Fermion excitations is played by the single-electron transitions between many-electron states. This is seen from the fact that switching on/off the mixing, (and/or hopping) between the upper transitions $|\Gamma_n\rangle \rightarrow |\Gamma_{n+1}\rangle$ and the delocalized states, leads to a deviation of the upper and lower spectral weights from zero or unity and make these weights non-integer numbers. Then, the Fermion GFs acquire a many-pole structure, where each pole contributes with its own weight. In turn, these weights are determined by the population numbers (of the type $N_{\Gamma_n} \sim \langle \tilde{n}_1\tilde{n}_2\ldots\tilde{n}_n(1-\tilde{n}_{n+1})(1-\tilde{n}_{n+2})\ldots(1-\tilde{n}_N)\rangle$, where N is the number of orbitals in the shell) of the many-electron states involved.

Third, the number of delocalized, correlated, orbitals (delocalized renormalized Fermions) does not obligatory coincide with the number of the single-electron transitions.

Fourth, a part of the many-electron states which are composed mainly of the localized orbitals, often form a (quasi)degenerate subsystem. Redistribution of spectral weights between the transitions involving these states may be caused by small energies.

Fifth, the spectral weights enter as factors to mixing, hopping, and Coulomb interaction, decreasing their strength and providing the correlation caused mechanism of band narrowing. Since these weights are determined by the strength of the interactions, the problem requires self-consistent solution which may reflect the competition between the Hund-rule interactions and the cohesive energy.

Sixth, the closed equations for the GFs of the Hubbard operators in terms of functional derivatives contain two types of contributions. One type is responsible for the description of effects from kinematic interactions originating from mixing and hopping (an example of the physics involved, the correlation mechanism of delocalization, see in Ref.[4]), another type generates an analogue of the WCPT for the Fermion GF. The series for the many-electron GFs obtained by neglecting the contributions from the kinematic interactions is isomorphic to the series for the single-electron Fermion GF in WCPT. Using this isomorphism, and comparing the Migdal-Galitskii formula for total energy of the non-correlated and correlated systems as well as the Sham equation for the exchange-correlation potential, we came to the conclusion that the form for the exchange-correlation potential used within weak-coupling theories can be used in the theory of the correlated systems also, if one will use the mixing, hopping, the inverse of the overlap matrix and the expression for charge density renormalized by many-electron spectral weights. The recipe for concrete calculations and example of such calculation is given in future works.

Seventh, the model Hubbard U can be expressed in terms of energies of transitions between many-electron states. Consideration of screening of these transitions by Coulomb interactions shows that the lower transitions are renormalized much weaker than the upper ones. This makes calculations within one parameter, $U^{\text{mod}}$, somewhat confusing, since they do not reflect the true picture.

Let us discuss this question in a more details, and make an attempt to elucidate what actually should be understood under Hubbard $U$ from the point of view of this many-electron theory. A commonly used definition of the Hubbard U has risen from the following speculation. The energy of the n-orbital atom modeled with the Hubbard model is

$$E_n = n\varepsilon_0^d + \frac{1}{2}n(n-1)U^{\text{mod}}.$$  \hspace{1cm} (102)

From this one finds that the energies of single-electron excitations are

$$\Delta_1 = E_n - E_{n-1} = \varepsilon_0^d + U^{\text{mod}}(n-1),$$ \hspace{1cm} (103)

$$\Delta_2 = E_{n+1} - E_n = \varepsilon_0^d + U^{\text{mod}}n$$  \hspace{1cm} (104)

and, therefore,

$$U^{\text{mod}} = \Delta_2 - \Delta_1.$$  \hspace{1cm} (105)

The parameter $\varepsilon_0$ can be taken from the requirement that the effective attractive potential is able to hold $n$ electrons (this is determined by the valence of the atom) and, therefore, $\varepsilon_0^d = -(n-1/2)U^{\text{mod}}$ and, in turn, $\Delta_1 = -U^{\text{mod}}/2$ and $\Delta_2 = U/2$. Thus, $\Delta_1$ and $\Delta_2$ play the role of the centers of the Hubbard sub bands. Hubbard used the Coulomb matrix element of density-density type for $U^{\text{mod}}$. According to the common opinion, it has unreasonably large values, between 20 and 30 eV for a d-shell, and, therefore, is considered irrelevant. In LDA+U calculations "reasonable" values of $U^{\text{mod}}$ for transition metals are near 5-8 eV, while in recent calculations, based on dynamical mean field theory, in order to obtain a reasonable agreement with the spectroscopical data for iron the authors had to take a value
of about 3 eV\textsuperscript{26}. There are, however, no suggestions what mechanism that is responsible for such a drastic decrease of \( U \) from 20 to 6 (or even to 3) eV. The common believe is that delocalization plus screening, particularly, due to interaction with some other bands, may provide such a decrease. It is easy to see, that at least, the density-density interaction with other bands does not change the picture. Indeed, let us imagine, that besides, say, a d-shell the atom also contains another shell with \( m \) atoms. If we add the term \( U_{cdmn} \) to the energy, it changes \( \Delta_1 \) and \( \Delta_2 \)

\[
\Delta_1 \Rightarrow \Delta_1 + U_{cdm}, \quad \Delta_2 \Rightarrow \Delta_2 + U_{cdm},
\]

(106)

but does not change \( U_{mod} \). \( \Delta_2 - \Delta_1 = U_{mod} \). Earlier\textsuperscript{22} we also investigated the influence of the delocalization on \( U_{mod} \) via renormalization by (kinematic) mixing interaction, it gives a decrease of at most 10\% under favorable conditions. Therefore, either other mechanisms should be involved or the description in terms of one parameter is oversimplified. From our consideration given above we can conclude that both assumptions are relevant.

First, it is important, which experiment we want to compare with. It is well-known that for \textit{ab initio} DFT LDA calculations the excited states with large energy of excitations are difficult since they usually involve non-single-electron excitation and the latter are not included into the effective single-electron Kohn-Sham scheme (even with different corrections). However, in low-energy experiments the lower Hubbard band is not involved. Therefore, for the description of such experiments one is interested only in the properties of the upper Hubbard band. The model calculation, which are trying to work with energies separated by a large scale, usually does not take into account self-consistent changes of the charge density. This involves the strongest interactions existing in the system. Therefore, it looks like only methods which combine the \textit{ab initio} methods with the many-body theory might be able to treat such problems. Within our many-electron approach the important parameters of the system are \( \Delta_1 \) and \( \Delta_2 \). They are connected with the model parameter Hubbard \( U \), however, they have, obviously, many-electron nature.

Second, there are two reasons why it is very important, where the levels \( \Delta_1 \) and \( \Delta_2 \) are situated with respect to all other bands and the chemical potential: a) this influences the distribution of spectral weights; b) the efficiency of screening depends on it. Actually, the lower the transition is under the Fermi level, the less the Coulomb interaction, via which it interacts with other electrons, is screened (see the speculations about the one loop contribution to the polarization operator, Eq.(78)).

Third, the way of calculation, obviously, depends on the reference point which interactions are included into \( \Delta_1^{(0)}, \Delta_1^{(4)} \). If we start with the LDA picture with a certain number of localized electrons, we have self-consistent \( f \)-wave functions, from them we can construct of the wave functions of the many-electron states, and calculate the energies \( E_{\Gamma_{n-1}}, E_{\Gamma_{n}}, E_{\Gamma_{n+1}} \) without any relaxation of charge. The differences of these energies provides \( \Delta_2^{(0)}, \Delta_1^{(0)} \). It should be emphasized that in this approach the LDA based calculation is used only as a generator of a convenient minimal set of wave functions for calculating \( E_{\Gamma_{n-1}}, E_{\Gamma_{n}}, E_{\Gamma_{n+1}} \). The energies themselves should be calculated on the basis of the many-electron states, \( |\Gamma\rangle \). Then, one can switch on mixing and hopping and take into account the screening and the renormalization of \( \Delta_2^{(0)}, \Delta_1^{(0)} \) via the self-energies of the many-electron GFs. Let us start with the lower transition. If we denote the Coulomb interaction between the localized and delocalized electrons as \( U_{id} \), delocalized-delocalized as \( U_{dd} \), it is clear that the largest contribution to self-energy for the renormalization of \( \Delta_1 \) comes from the graphs which contain the lowest possible number of interactions \( U_{id} \), because, as we have seen in previous section, each loop constructed on \( U_{id} \) involves the loop with large denominator of the order of \( \Delta_2 - \Delta_1 = U_{mod} \). Therefore, the largest contribution to the self-energy with density-density matrix elements \( U_{dd} \), renormalizing the lower transition, contains \( U_{id} \) only twice (see the graph in Fig.\textsuperscript{[4]} and Fig.\textsuperscript{[3]}). Strictly speaking, the equations for the lower (and for upper as well) GFs always form a system of equations,

\[
G^{a_1\bar{a}_1'}(i\omega) = G_0^{a_1\bar{a}_1'}(i\omega) + G_0^{a_1\bar{a}_1'}(i\omega)\Sigma_{a_2\bar{a}_4}^H + T\sum_{\omega_1} \bar{v}_{a_2\bar{a}_3a_5} \Pi_{\Delta_1\omega_1} (i\omega - i\omega_1) \\
x \bar{v}_{a_2\bar{a}_3\bar{a}_4} G^{a_2\bar{a}_3}(i\omega_1) G^{a_4\bar{a}_1'}(i\omega),
\]

(107)

where \( \Sigma_{a_2\bar{a}_4}^H \) is the Hartree contribution and \( \Pi \) is the full polarization operator. However, if we neglect the differences between the levels \( \Delta_1 \), we can write the equation for renormalized \( \Delta_1 \):

\[
\Delta_1(i\omega) = \Delta_1^{(0)} + \alpha T \sum_{\omega_1} \bar{v}_{a_1\bar{a}_2a_5} \Pi_{\Delta_1\omega_1} (i\omega - i\omega_1) \\
x \bar{v}_{a_1\bar{a}_2\bar{a}_3} G^{a_1\bar{a}_1'} (i\omega_1),
\]

(108)

where \( \alpha \) takes into account the number of internal transitions, \( a_5 \) in Eq.(107). The situation with the upper transition is more complex since in this region the bands are formed. For this reason it can be defined via the static dielectric
permeability as a solution of the equation with Hartree and, screened by static $\varepsilon^{-1}$, exchange interaction, i.e. in the Eq. (107) using instead of the second term with $\varepsilon^{-1}(0)$ and $F$ and $v$ replaced by $G$ and $\bar{v}$. As we see, the self-consistent magnitudes $\Delta_2, \Delta_1$ become frequency-dependent already in the first steps of their dressing by electron-hole excitations. This makes such calculations quite cumbersome and practically difficult. The other possible way would be to calculate, as described above, the non-self-consistent values of $\Delta_2^{(0)}, \Delta_1^{(0)}$ and to treat them as the input parameters for further LDA calculations, where they will be renormalized as centers of bands usually do.

In conclusion, we have reported the following results. The perturbation theory for correlated electron systems developed in previous paper here is extended to the case of Coulomb interaction. It is shown in the level of closed functional equations for the many-electron Green functions that all the contributions in SCPT can be separated to two classes. One of them forms the approximation of renormalized fermions, ARF, does not include kinematic interactions, and is fully analogous to the WCPT for single-electron GFs. Another one includes them and, therefore, contains specific for CES effects. The ARF is used for formulation of simple recipe for extension of the LDA to DFT to the case of strongly correlated electrons. The application to rare earths is given in next paper.

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APPENDIX A: THE COULOMB TERMS IN EQUATIONS OF MOTION FOR GREEN FUNCTIONS

Class 0. This class belongs to the ones considered above. Nevertheless, for completeness we give the detailed formulas. The correction to the EM for the GF $\langle Tc_1(t)\eta^i(t')\rangle_u$ ($\eta$ is either a $c$ or a $X$ operator) from the interaction between the conduction electrons is

$$V_{1,3,4,5,6} \langle T_{c_3^1}(t)c_4^1(t)c_5^1(t)\eta^i(t')\rangle_u = V_{1,3,4,5,6} \lim_{t_1 \rightarrow t+0} \left[ \langle T_{c_3^1}(t_1)c_4^1(t_1) \rangle + i\frac{\delta}{\delta U_{34}^{cc}(t_1)} \right] \times \langle Tc_5(t)\eta^i(t')\rangle_u, \quad (A1)$$

while the GFs generated by the commutator $[X, V_6]$ can be expressed as follows

$$\langle T_{Z_{j_1}^{c_i}}(t)c_3^1(t)c_4^1(t)c_5^1(t)\eta^i(t')\rangle_u = \lim_{t_1 \rightarrow t+0} \left[ \langle T_{Z_{j_1}^{c_i}}(t_1) \rangle + i\frac{\delta}{\delta U_{34}^{cc}(t_1)} \right] \times \langle Tc_3^1(t_1)c_4^1(t_1)\eta^i(t')\rangle_u, \quad (A2)$$

$$\times \lim_{t_2 \rightarrow t_1+0} \left[ \langle T_{Z_{j_1}^{c_i}}(t_2) \rangle + i\frac{\delta}{\delta U_{34}^{cc}(t_2)} \right] \times \langle Tc_3^1(t_2)c_4^1(t_2)\eta^i(t')\rangle_u. \quad (A3)$$

Below, for brevity, we shall denote the time limits by upper index ”plus”:

$$\lim_{t_2 \rightarrow t_1+0} R(t_2) \equiv R(t_1^+). \quad (A4)$$

Further,

$$\langle TX_{j_i}^{d_i}(t)c_4^1(t)c_5^1(t)\eta^i(t')\rangle_u = \langle TX_{j_i}^{d_i}(t^+)c_4^1(t^+)\rangle_u + i\frac{\delta}{\delta U_{j_i,d_i}^{cc}(t^+)} \times \langle Tc_5(t)\eta^i(t')\rangle_u. \quad (A5)$$
Then in the Hartree approximation we have to neglect the contribution from this derivative. We shall use the notation \( \delta^{(1)} G_{1c}^{(c)} \) for the right-hand side contribution to the EM for corresponding GF, not for the GF itself. Thus, for the GF \( (1/i) \langle T c_1(t) \eta(t') \rangle_u = G_{1c}^{(c)} \) we have the standard expression

\[
\delta^{(1)} G_{1c}^{(c)} = V_{1,3,4,5,6} \langle T c_1^\dagger(t_1) c_4(t_1) \rangle \langle T c_5(t) \eta(t') \rangle_u,
\]

where \( V_{1,3,4,5,6} = O_{1,2}^{-1} v_{2,3,4,5,6} \). The index (0) means that the correction comes from the class 0. This is, obviously, the standard Hartree correction. The exchange-correction comes from the derivative, next,

\[
\delta^{(1)} G_{1c}^{(c)} = v_{[2,3,4,5,6]} O_{1,2,3,4,5}^{-1} \langle f_2 \rangle \delta^{a_1 a_2} \langle T Z_{\xi_1}^f (t') \rangle_u \\
\times \langle T c_5(t) \eta(t') \rangle_u \\
+ \frac{1}{2} v_{[2,3,4,5,6]} O_{1,2,3,4,5}^{-1} \langle f_2 \rangle \delta^{a_1 a_2} \langle T Z_{\xi_1}^f (t') \rangle_u \\
\times \langle T c_5(t) \eta(t') \rangle_u.
\]

\[
\text{Class 1.} \text{ The first GF arising from the } c \text{-operator is } \langle T Z^f c c \eta \rangle \text{ which is considered above. The other functions coming from } [c_1, \hat{V}_1] \text{ are}
\]

\[
\langle T X_{\xi_1}^{a_2} (t) c_4(t) c_5(t) \eta(t') \rangle_u \\
= \left[ \langle T X_{\xi_1}^{a_2} (t) c_4(t) \rangle_u + i \frac{\delta}{\delta U^{X_{\xi_1}^{a_2} (t')}} \right] \\
\times \langle T c_5(t) \eta(t') \rangle_u,
\]

(A8)

and

\[
\langle T c_5(t) X_{\xi_1}^{a_2} (t) c_5(t) \eta(t') \rangle_u \\
= \left[ \langle T c_5(t) X_{\xi_1}^{a_2} (t) \rangle_u + i \frac{\delta}{\delta U^{X_{\xi_1}^{a_2} (t')}} \right] \\
\times \langle T c_5(t) \eta(t') \rangle_u.
\]

(A9)

The functions which come from \([c_1, \hat{V}_1]\) we rewrite as

\[
\delta^{(1)} G_{1c}^{(c)} = v_{[2,3,4,5,6]} \langle f_2 \rangle \delta^{a_1 a_2} \langle T Z_{\xi_1}^f (t') \rangle_u \\
+ \frac{i}{\delta U^{X_{\xi_1}^{a_2} (t')}} \\
\times \langle T c_3(t) \eta(t') \rangle_u + i \frac{\delta}{\delta U^{X_{\xi_1}^{a_2} (t')}} \langle T c_5(t) \eta(t') \rangle_u \\
+ v_{[2,3,4,5,6]} \langle f_2 \rangle \delta^{a_1 a_2} \langle T Z_{\xi_1}^f (t') \rangle_u \\
\times \langle T c_5(t) \eta(t') \rangle_u \\
+ \frac{i}{\delta U^{X_{\xi_1}^{a_2} (t')}} \\
\times \langle T c_3(t) \eta(t') \rangle_u + i \frac{\delta}{\delta U^{X_{\xi_1}^{a_2} (t')}} \langle T c_5(t) \eta(t') \rangle_u.
\]

(A10)

Therefore, the Hartree contribution is

\[
\delta^{(1)} G_{1c}^{(c)} = v_{[2,3,4,5,6]} \langle f_2 \rangle \delta^{a_1 a_2} \langle T Z_{\xi_1}^f (t') \rangle_u \\
\times \langle T c_3(t) \eta(t') \rangle_u + i \frac{\delta}{\delta U^{X_{\xi_1}^{a_2} (t')}} \\
\times \langle T c_5(t) \eta(t') \rangle_u \\
+ v_{[2,3,4,5,6]} \langle f_2 \rangle \delta^{a_1 a_2} \langle T Z_{\xi_1}^f (t') \rangle_u \\
\times \langle T c_5(t) \eta(t') \rangle_u.
\]

(A11)
The contribution to the GF $\langle TX^\eta \rangle$ is

$$\delta^{(1)} G_{j_1a_1}^{(X^\eta)} = v_{[j_2,j_3]} e_\xi \xi \varepsilon^{\tilde{a}_1\tilde{a}_2} (f^\dagger_2 \tilde{a}_2) \delta_{j_1,j_2} \langle T Z^\xi_{j_3} (t^+) \rangle_u$$

$$+ \frac{i}{\delta U_{j_1j_1}(t^+)} \langle (T_{c_5}^\dagger (t^+) c_4 (t^+) \rangle_u + i \frac{\delta}{\delta U_{\xi,4}^c (t^+)} \langle T_{c_5} (t) \eta^\dagger (t') \rangle_u$$

$$+ v_{[j_2,j_3]} e_\xi \xi \varepsilon^{\tilde{a}_1\tilde{a}_2} (f^\dagger_2 \tilde{a}_2) \delta_{j_1,j_2} \langle T Z^\xi_{j_3} (t^+) \rangle_u$$

$$+ \frac{i}{\delta U_{j_1j_1}(t^+)} \langle (T X^b_{j_2} (t^+) c_4 (t^+) \rangle_u + i \frac{\delta}{\delta U_{j_1j_1}(t^+)} \langle T_{c_5} (t) \eta^\dagger (t') \rangle_u$$

$$+ v_{[j_2,j_3]} e_\xi \xi \varepsilon^{\tilde{a}_1\tilde{a}_2} (f^\dagger_2 \tilde{a}_2) \delta_{j_1,j_2} \langle T Z^\xi_{j_3} (t^+) \rangle_u$$

$$\times \langle (T_{c_5}^\dagger (t^+) X^a_{j_4} (t^+) \rangle_u + i \frac{\delta}{\delta U_{\xi,4}^c (t^+)} \langle T_{c_5} (t) \eta^\dagger (t') \rangle_u$$

$$+ v_{[j_2,j_3]} e_\xi \xi \varepsilon^{\tilde{a}_1\tilde{a}_2} (f^\dagger_2 \tilde{a}_2) \delta_{j_1,j_2} \langle T Z^\xi_{j_3} (t^+) \rangle_u$$

$$\times \langle (T_{c_5}^\dagger (t^+) X^a_{j_4} (t^+) \rangle_u + i \frac{\delta}{\delta U_{j_1j_1}(t^+)} \langle T_{c_5} (t) \eta^\dagger (t') \rangle_u$$

$$\times \langle T_{c_5} (t) \eta^\dagger (t') \rangle_u \rangle_u \}.$$  (A12)

The corresponding Hartree part is

$$\delta^{(1)} G_{j_1a_1}^{(X^\eta)} = v_{[j_2,j_3]} e_\xi \xi \varepsilon^{\tilde{a}_1\tilde{a}_2} (f^\dagger_2 \tilde{a}_2) \delta_{j_1,j_2} \langle T Z^\xi_{j_3} (t^+) \rangle_u$$

$$\times \langle (T_{c_5}^\dagger (t^+) c_4 (t^+) \rangle_u \langle T_{c_5} (t) \eta^\dagger (t') \rangle_u$$

$$+ v_{[j_2,j_3]} e_\xi \xi \varepsilon^{\tilde{a}_1\tilde{a}_2} (f^\dagger_2 \tilde{a}_2) \delta_{j_1,j_2} \langle T Z^\xi_{j_3} (t^+) \rangle_u$$

$$\times \langle (T X^b_{j_2} (t^+) c_4 (t^+) \rangle_u \langle T_{c_5} (t) \eta^\dagger (t') \rangle_u$$

$$+ v_{[j_2,j_3]} e_\xi \xi \varepsilon^{\tilde{a}_1\tilde{a}_2} (f^\dagger_2 \tilde{a}_2) \delta_{j_1,j_2} \langle T Z^\xi_{j_3} (t^+) \rangle_u$$

$$\times \langle (T_{c_5}^\dagger (t^+) X^a_{j_4} (t^+) \rangle_u \langle T_{c_5} (t) \eta^\dagger (t') \rangle_u$$

$$+ v_{[j_2,j_3]} e_\xi \xi \varepsilon^{\tilde{a}_1\tilde{a}_2} (f^\dagger_2 \tilde{a}_2) \delta_{j_1,j_2} \langle T Z^\xi_{j_3} (t^+) \rangle_u$$

$$\times \langle (T_{c_5}^\dagger (t^+) X^a_{j_4} (t^+) \rangle_u \langle T_{c_5} (t) \eta^\dagger (t') \rangle_u$$

$$+ v_{[j_2,j_3]} e_\xi \xi \varepsilon^{\tilde{a}_1\tilde{a}_2} (f^\dagger_2 \tilde{a}_2) \delta_{j_1,j_2} \langle T Z^\xi_{j_3} (t^+) \rangle_u$$

$$\times \langle (T_{c_5}^\dagger (t^+) X^a_{j_4} (t^+) \rangle_u \langle T_{c_5} (t) \eta^\dagger (t') \rangle_u$$

$$+ v_{[j_2,j_3]} e_\xi \xi \varepsilon^{\tilde{a}_1\tilde{a}_2} (f^\dagger_2 \tilde{a}_2) \delta_{j_1,j_2} \langle T Z^\xi_{j_3} (t^+) \rangle_u$$

$$\times \langle (T_{c_5}^\dagger (t^+) X^a_{j_4} (t^+) \rangle_u \langle T_{c_5} (t) \eta^\dagger (t') \rangle_u \rangle_u \}.$$  (A13)

Class 2. Here the corrections to the equations of motion are

$$\delta^{(2)} G_{j_1}^{(en)} = \frac{1}{2} v_{[j_2,j_3]} e_\xi \xi \varepsilon^{\tilde{a}_1\tilde{a}_2} (f^\dagger_2 \tilde{a}_2) \delta_{j_2,j_3} \langle T Z^\xi_{j_3} (t^+) \rangle_u$$

$$\times \langle (T_{c_5}^\dagger (t^+) c_4 (t^+) \rangle_u \langle T_{c_5} (t) \eta^\dagger (t') \rangle_u$$

$$+ v_{[j_2,j_3]} e_\xi \xi \varepsilon^{\tilde{a}_1\tilde{a}_2} (f^\dagger_2 \tilde{a}_2) \delta_{j_2,j_3} \langle T Z^\xi_{j_3} (t^+) \rangle_u$$

$$\times \langle (T X^b_{j_2} (t^+) c_4 (t^+) \rangle_u \langle T_{c_5} (t) \eta^\dagger (t') \rangle_u$$

$$+ v_{[j_2,j_3]} e_\xi \xi \varepsilon^{\tilde{a}_1\tilde{a}_2} (f^\dagger_2 \tilde{a}_2) \delta_{j_2,j_3} \langle T Z^\xi_{j_3} (t^+) \rangle_u$$

$$\times \langle (T_{c_5}^\dagger (t^+) X^a_{j_4} (t^+) \rangle_u \langle T_{c_5} (t) \eta^\dagger (t') \rangle_u$$

$$+ v_{[j_2,j_3]} e_\xi \xi \varepsilon^{\tilde{a}_1\tilde{a}_2} (f^\dagger_2 \tilde{a}_2) \delta_{j_2,j_3} \langle T Z^\xi_{j_3} (t^+) \rangle_u$$

$$\times \langle (T_{c_5}^\dagger (t^+) X^a_{j_4} (t^+) \rangle_u \langle T_{c_5} (t) \eta^\dagger (t') \rangle_u$$

$$\times \langle T_{c_5} (t) \eta^\dagger (t') \rangle_u \rangle_u \}.$$  (A14)
\*[(TX^b_{j_2}(t^+)c_4(t^+))_u + \frac{\delta}{\delta U^{X_c}_{j_2,b,4_c}(t^+)}(TC_5(t)\eta^1(t'))_u]
\*[(TX^{a_3}_{j_3}(t^+)c_4(t^+))_u + \frac{\delta}{\delta U^{X_c}_{j_3,a_3,4_c}(t^+)}(TC_5(t)\eta^1(t'))_u]
\*[(TX^{a_2}_{j_2}(t^+)c_4(t^+))_u + \frac{\delta}{\delta U^{X_c}_{j_2,a_2,4_c}(t^+)}(TC_5(t)\eta^1(t'))_u]

(A14)

\(\delta(2) G^{(X\eta)}_{j_1,a_1} = \frac{1}{2} v_{j_2,j_3,a_3,5_c} \sum_{j_2,j_3} \{ \delta_{j_2,j_3}(f_{j_2}^f f_{j_3}^f)^\eta_b \}
\*[(TX^{a_2}_{j_2}(t^+)c_4(t^+))_u + \frac{\delta}{\delta U^{X_c}_{j_2,a_2,4_c}(t^+)}(TC_5(t)\eta^1(t'))_u]
\*[(TX^{a_2}_{j_2}(t^+)c_4(t^+))_u + \frac{\delta}{\delta U^{X_c}_{j_2,a_2,4_c}(t^+)}(TC_5(t)\eta^1(t'))_u]
\*[(TX^{a_2}_{j_2}(t^+)c_4(t^+))_u + \frac{\delta}{\delta U^{X_c}_{j_2,a_2,4_c}(t^+)}(TC_5(t)\eta^1(t'))_u]

(A15)

The remaining contributions, in this class, comes from the processes of transforming two c- into f-electrons

\(\delta(2) G^{(f^f)}_{j_1,a_1} = \frac{1}{2} v_{j_2,j_3,a_3,5_c} \sum_{j_2,j_3} \{ \delta_{j_2,j_3}(f_{j_2}^f f_{j_3}^f)^\eta_b \}
\*[(TX^b_{j_2}(t^+)c_4(t^+))_u + \frac{\delta}{\delta U^{X_c}_{j_2,b,4_c}(t^+)}(TC_5(t)\eta^1(t'))_u]
\*[(TX^b_{j_2}(t^+)c_4(t^+))_u + \frac{\delta}{\delta U^{X_c}_{j_2,b,4_c}(t^+)}(TC_5(t)\eta^1(t'))_u]
\*[(TX^b_{j_2}(t^+)c_4(t^+))_u + \frac{\delta}{\delta U^{X_c}_{j_2,b,4_c}(t^+)}(TC_5(t)\eta^1(t'))_u]

(A16)
Thus, these two corrections differ only by factors of the overlap matrixes coming from the commutator of c-operator with interaction. Class 2, 3e). Indeed, a c-operator, located on site $j_1$ "feels" strong correlations on other site $j_2$ only due to non-orthogonality, i.e. due to the f-component which it contains on the site $j_2$. Remaining terms in this class come from the interaction 3f, where two f-electrons are transformed to c-electrons:

$$\delta^{(2)}G_{1c}^{ff} = \nu_{2c,3c}|4f_5\rangle O^{-1}_{j_1,2c}(f_4 f_5)^\eta \{\delta_{j_4 j_5} \langle t \rangle c_{\eta} \xi \rangle_{\eta} + i \frac{\delta}{\delta U_{j_4 j_5}} \langle t \rangle c_{\eta} \xi \rangle_{\eta}\} \times \langle T X^a_{3c}(t) c_{\eta} \xi \rangle_{\eta} \langle t \rangle,$$

(A17)

and

$$\delta^{(2)}G_{j_1 a_1}^{ff} = \nu_{2c,3c}|4f_5\rangle O^{-1}_{j_1,2c}(f_4 f_5)^\eta \{\delta_{j_4 j_5} \langle t \rangle c_{\eta} \xi \rangle_{\eta} + i \frac{\delta}{\delta U_{j_4 j_5}} \langle t \rangle c_{\eta} \xi \rangle_{\eta}\} \times \langle T X^a_{3c}(t) c_{\eta} \xi \rangle_{\eta} \langle t \rangle,$$

(A19)

We see that new types of GFs, $\langle T c_{j_4}^i Z^a_{j_3}(\eta) c_{\eta} \rangle_{\eta}$, have appeared which cannot be decoupled in a standard way. Expectation values of the type $\langle T c_{j_4}^i(\eta) c_{\eta} \rangle_{\eta}$ or $\langle T Z^a_{j_3}(t) \rangle_{\eta}$ are equal to zero in the equilibrium non-superconducting state. In the external fields $\int dt U(t) Z^a(t)$, they do exist. Therefore, we should keep these expectation values while the fields are not equal to zero and after calculation of the derivatives $\delta \langle T Z^a_{j_3}(t) \rangle_{\eta}$ and $\delta \langle T c_{j_4}^i(t) c_{\eta} \rangle_{\eta}$, etc., we can put them equal to zero. Usually these graphs give small contributions since they involve the gap $\sim U$ in the denominator. However, these contributions describe the an effective antiferromagnetic interaction between (quasi)localized electrons and, therefore, without their contributions it is difficult to obtain localized antiferromagnetism at all. Thus, we can use, for example, the decoupling

$$\langle T c_{j_4}^i Z^a_{j_3}(t) \rangle_{\eta} \langle t \rangle = [(Z^a_{j_3}(t^+)) + i \frac{\delta}{\delta U_{j_3 j_4}}(t^-)] \langle T c_{j_4}^i(t) \rangle_{\eta} \langle t \rangle.$$

(A20)

The direct derivative of the zero inverted GF, $\langle T c_{j_4}^i(t) \rangle_{\eta} \langle t \rangle^{-1}$, is equal to zero. However, it is always connected in the equations of motion with the operators $cZ^a(t)$ that gives the non-zero loop correction from $\langle T c_{j_4}^i(t) c_{\eta} \rangle_{\eta} \langle T Z^a_{j_3}(t) \rangle_{\eta}$.

Class 3. The terms, containing three $f$-operators may have the operators, belonging to the same site, or to different ones. If they belong to the same site, we can write them as follows

$$v_{2c,3c} \nu_{4f_5} \{\delta_{j_4 j_5} \langle f_4 f_5 \rangle \langle t \rangle c_{\eta} \xi \rangle_{\eta} + \nu_{2c,3c} \nu_{4f_5} \{\delta_{j_4 j_5} \langle f_4 f_5 \rangle \langle t \rangle c_{\eta} \xi \rangle_{\eta} \langle t \rangle,$$

(A21)
They, obviously, also belong to mixing interaction and have been included to it in Ref.\[1\]

Next are the terms containing two \(f\)-operators, one of them belonging to one site, and another one to other site. They can be written as follows:

\[
\delta^{(3)}G_{t_c}^{ff} = v_{2,3,4,5} \delta_{j_0j_1} \delta_{j_2j_3} \langle f_2^\dagger f_3 f_4 \rangle \langle T \rangle \xi_t^3 \\
\times \{ O_{1,2} \langle f_2 \rangle a_i^a \langle f_3 \rangle b \langle f_4 \rangle c \langle Z_{j_2}^3 \rangle + i \frac{\delta}{\delta U_{j_2}^3 \xi_t^3} \} \\
\times \{ \langle Z_{j_3}^3(t^+) \rangle \langle T \rangle c_5(t) \eta(t^+) \} + \frac{\delta}{\delta U_{j_3}^3 \xi_t^3} \langle T \rangle c_5(t) \eta(t^+) \\
- O_{1,2} \langle f_3 \rangle a_i^a \langle f_4 \rangle b \langle f_5 \rangle c \langle T \rangle X_{j_2}^3(t^+) X_{j_3}^b(t^+) \\
+ i \frac{\delta}{\delta U_{j_3}^3 \xi_t^3} \langle T \rangle X_{j_3}^b(t) \eta(t^+) \}.
\]

(A22)

Then, for the GF \( \langle T X_{j_1}^a(t) \eta(t^+) \rangle \) we have

\[
\delta^{(3)}G_{j_0 j_1}^{j_1 f} = v_{2,3,4,5} \delta_{j_0j_1} \delta_{j_2j_3} \langle f_2^\dagger f_3 f_4 \rangle \langle T \rangle \xi_t^3 \\
\times \{ O_{1,2} \langle f_2 \rangle a_i^a \langle f_3 \rangle b \langle f_4 \rangle c \langle Z_{j_1}^3 \rangle + i \frac{\delta}{\delta U_{j_1}^3 \xi_t^3} \} \\
\times \{ \langle Z_{j_3}^3(t^+) \rangle \langle T \rangle c_5(t) \eta(t^+) \} + \frac{\delta}{\delta U_{j_3}^3 \xi_t^3} \langle T \rangle c_5(t) \eta(t^+) \\
- \delta_{j_1j_3} \langle f_3 \rangle a_i^a \langle T \rangle X_{j_2}^3(t^+) X_{j_3}^b(t^+) \\
+ i \frac{\delta}{\delta U_{j_3}^3 \xi_t^3} \langle T \rangle X_{j_3}^b(t) \eta(t^+) \}.
\]

(A23)

Class 4. Since the terms, which contain four \(f\)-operators and belong to the same site, are included into the definition of the on-site energies \( E_\Gamma \) of the terms \( \Gamma \), we start with the density-density interaction between different sites:

\[
\delta^{(4)}G_{t_c}^{ff} = \frac{1}{2} v_{2,3,4,5} \delta_{j_0j_1} \delta_{j_2j_3} \delta_{j_4j_5} \langle f_2^\dagger f_3 f_4 \rangle \langle f_5 \rangle \langle T \rangle \xi_t^3 \\
\times \{ O_{1,2} \langle f_2 \rangle a_i^a \langle f_3 \rangle b \langle f_4 \rangle c \langle Z_{j_1}^3 \rangle + i \frac{\delta}{\delta U_{j_1}^3 \xi_t^3} \} \\
\times \{ \langle Z_{j_3}^3(t^+) \rangle \langle T \rangle c_5(t) \eta(t^+) \} + \frac{\delta}{\delta U_{j_3}^3 \xi_t^3} \langle T \rangle c_5(t) \eta(t^+) \\
+ O_{1,2} \langle f_3 \rangle a_i^a \langle f_4 \rangle b \langle f_5 \rangle c \langle T \rangle X_{j_2}^3(t^+) X_{j_3}^b(t^+) \\
+ i \frac{\delta}{\delta U_{j_3}^3 \xi_t^3} \langle T \rangle X_{j_3}^b(t) \eta(t^+) \}.
\]

(A24)
At last, the corrections to the EM from single-particle and atom with spin less electrons. This electron shell can be described by the Hamiltonian: 

\[ H = \sum_{\text{orbital}} \varepsilon_{\text{orbital}} \hat{n}_{\text{orbital}} + U \sum_{m \neq m'} \hat{n}_m \hat{n}_{m'} \]

where \( \varepsilon_0 \) describes the attraction to the nuclear potential which provides the ground state with two bonded electrons.

The Hamiltonian has the following eigenstates and eigenvalues

| \( n \) state | \( E_n \) |
|--------------|------|
| 0 \( |0\rangle = |000\rangle \) | 0 |
| 1 \( d_{1z}^2 |0\rangle = |100\rangle \) | \(-\frac{3}{2}U\) |
| 1 \( d_{2z}^2 |0\rangle = |010\rangle \) | \(-\frac{3}{2}U\) |
| 1 \( d_{3z}^2 |0\rangle = |001\rangle \) | \(-\frac{3}{2}U\) |
| 2 \( d_{1z}^1 d_{2z}^1 |0\rangle = |110\rangle \) | \(-2U\) |
| 2 \( d_{2z}^1 d_{3z}^1 |0\rangle = |011\rangle \) | \(-2U\) |
| 2 \( d_{3z}^1 d_{4z}^1 |0\rangle = |101\rangle \) | \(-2U\) |
| 3 \( d_{1z}^1 d_{2z}^1 d_{3z}^1 |0\rangle = |111\rangle \) | \(-\frac{5}{2}U\) |

Introducing the Hubbard operators \( |i \rangle \langle j | = (1 - \delta_{ij})X_{ij} + \delta_{ij}h^i \) in terms of these states we diagonalize the Hamiltonian

\[ H = -\frac{3}{2}U[\hat{h}^{100} + \hat{h}^{010} + \hat{h}^{001} + \hat{h}^{111}] \]

\[ -2U[\hat{h}^{110} + \hat{h}^{011} + \hat{h}^{101}] \]

APPENDIX B: SPECTRAL WEIGHT TRANSFER: AN EXAMPLE OF TWO LOCALIZED ELECTRONS IN THREE-ORBITAL ATOMS.

The LDA+U and self-interaction correction methods are used in DFT for creating an orbital polarization, which allows to describe localized and delocalized electrons with different potentials. In this section we illustrate the mechanism of orbital polarization generated by strong intra-atomic interactions considering the example of an ion with 2 localized f-electrons. In order to make consideration more transparent we consider a hypothetical 3-orbital atom with spin less electrons. This electron shell can be described by the Hamiltonian:

\[ \mathcal{H} = \mathcal{H}_d + \mathcal{H}_{dd} = \sum_{m} \varepsilon_0 \hat{n}_m + U \sum_{m \neq m'} \hat{n}_m \hat{n}_{m'} \]

where \( m, m' = 1, 2, 3 \) and \( \hat{n}_m \equiv d_{m}^+ d_{m} \). The parameter \( \varepsilon_0 \) describes the attraction to the nuclear potential which provides the ground state with two bonded electrons

\[ E_n = \varepsilon_0 n + \frac{1}{2} Un(n-1), \quad \frac{dE_n}{dn} \bigg|_{n=2} = 0 \Rightarrow \varepsilon_0 = -\frac{3}{2}U \]

The Hamiltonian has the following eigenstates and eigenvalues

| \( n \) state | \( E_n \) |
|--------------|------|
| 0 \( |0\rangle = |000\rangle \) | 0 |
| 1 \( d_{1z}^2 |0\rangle = |100\rangle \) | \(-\frac{3}{2}U\) |
| 1 \( d_{2z}^2 |0\rangle = |010\rangle \) | \(-\frac{3}{2}U\) |
| 1 \( d_{3z}^2 |0\rangle = |001\rangle \) | \(-\frac{3}{2}U\) |
| 2 \( d_{1z}^1 d_{2z}^1 |0\rangle = |110\rangle \) | \(-2U\) |
| 2 \( d_{2z}^1 d_{3z}^1 |0\rangle = |011\rangle \) | \(-2U\) |
| 2 \( d_{3z}^1 d_{4z}^1 |0\rangle = |101\rangle \) | \(-2U\) |
| 3 \( d_{1z}^1 d_{2z}^1 d_{3z}^1 |0\rangle = |111\rangle \) | \(-\frac{5}{2}U\) |

Introducing the Hubbard operators \( |i \rangle \langle j | = (1 - \delta_{ij})X_{ij} + \delta_{ij}h^i \) in terms of these states we diagonalize the Hamiltonian

\[ \mathcal{H} = -\frac{3}{2}U[\hat{h}^{100} + \hat{h}^{010} + \hat{h}^{001} + \hat{h}^{111}] \]

\[ -2U[\hat{h}^{110} + \hat{h}^{011} + \hat{h}^{101}] \]

(28)
The Fermion operators in terms of Hubbard ones are

\[ d_1 = (000|d_1|100)X^{000,100} + (010|d_1|110)X^{010,110} \]
\[ + (001|d_1|101)X^{001,101} + (011|d_1|111)X^{011,111} \]
\[ = X^{000,100} + X^{010,110} + X^{001,101} + X^{011,111}, \]  

(B4)

\[ d_2 = X^{000,010} - X^{100,110} + X^{001,011} - X^{101,111}, \]  

(B5)

\[ d_3 = X^{000,001} - X^{100,101} - X^{010,011} + X^{110,111}. \]  

(B6)

Correspondently, the Fermion GFs are

\[ F_{11}(i\omega) = \langle T d_1(\tau)d_1^\dagger(\tau') \rangle_{i\omega} \]
\[ = \frac{1}{i} \langle T (X^{000,100} + X^{010,110} + X^{001,101} + X^{011,111}) \]
\[ \times (X^{100,000} + X^{110,010} + X^{101,001} + X^{111,011}) \rangle_{i\omega} \]
\[ = \frac{1}{i} \langle T X^{000,100}(\tau)X^{100,000}(\tau') \rangle_{i\omega} \]
\[ + \frac{1}{i} \langle T (X^{010,110}(\tau)X^{110,010}(\tau')) \rangle_{i\omega} \]
\[ + \frac{1}{i} \langle T X^{001,101}(\tau)X^{101,001}(\tau') \rangle_{i\omega} \]
\[ + \frac{1}{i} \langle T X^{011,111}(\tau)X^{111,011}(\tau') \rangle_{i\omega} \]
\[ = -i \frac{N_{000} + N_{100}}{i\omega + \frac{U}{2} + \mu} - i \frac{N_{010} + N_{110}}{i\omega + \frac{2U}{3} + \mu} \]
\[ -i \frac{N_{001} + N_{101}}{i\omega + \frac{U}{2} + \mu} - i \frac{N_{011} + N_{111}}{i\omega - \frac{2U}{3} + \mu} \].  

(B7)

The non-diagonal GF like \( \frac{1}{i} \langle T (X^{011,111}(\tau)X^{111,011}(\tau')) \rangle_{i\omega} \) = 0 due to the diagonal form of the Hamiltonian in this representation. In the same fashion

\[ F_{22}(i\omega) = \langle T d_2(\tau)d_2^\dagger(\tau') \rangle_{i\omega} \]
\[ = -i \frac{N_{000} + N_{010}}{i\omega + \frac{U}{2} + \mu} - i \frac{N_{100} + N_{110}}{i\omega + \frac{2U}{3} + \mu} \]
\[ -i \frac{N_{001} + N_{011}}{i\omega + \frac{U}{2} + \mu} - i \frac{N_{010} + N_{111}}{i\omega - \frac{2U}{3} + \mu} \].  

(B8)

\[ F_{33}(i\omega) = \langle T d_3(\tau)d_3^\dagger(\tau') \rangle_{i\omega} \]
\[ = -i \frac{N_{000} + N_{001}}{i\omega + \frac{U}{2} + \mu} - i \frac{N_{100} + N_{101}}{i\omega + \frac{2U}{3} + \mu} \]
\[ -i \frac{N_{010} + N_{011}}{i\omega + \frac{U}{2} + \mu} - i \frac{N_{101} + N_{111}}{i\omega - \frac{2U}{3} + \mu} \].  

(B9)

The population numbers in the numerators for the non-interacting atoms are just the Gibbs weights,

\[ N_{000} = 1/Z_0, \quad N_{100} = N_{010} = N_{010} = e^{\beta(\mu + \frac{U}{2})}/Z_0, \]
\[ N_{110} = N_{011} = N_{101} = e^{\beta(2\mu + 2U)}/Z_0, \]
\[ N_{111} = e^{\beta(3\mu + \frac{U}{2})}/Z_0, \]
\[ Z_0 = 1 + 3e^{\beta(\mu + \frac{U}{2})} + 3e^{\beta(2\mu + 2U)} + e^{\beta(3\mu + \frac{U}{2})}. \]  

(B10)

The chemical potential has to provide that the total number of electrons in the ion equals two. The equation for the number of electrons in this ion,
or written in terms of the many-electron population numbers, 

\[
\begin{align*}
n_d &= 0 \cdot N_{000} + 1 \cdot (N_{100} + N_{010} + N_{001}) \\
&+ 2 \cdot (N_{110} + N_{011} + N_{101}) + 3 \cdot N_{111} \\
&= \frac{3 e^{\beta (\mu + \frac{U}{2})} + 6 e^{\beta (2\mu + 2U)} + 3 e^{\beta (3\mu + 3U)}}{1 + 3 e^{\beta (\mu + \frac{U}{2})} + 3 e^{\beta (2\mu + 2U)} + e^{\beta (3\mu + 3U)}} = 2, \tag{B12}
\end{align*}
\]

can be fulfilled for \( \mu \) in the interval: \( \Delta_1 = E_2 - E_1 = -\frac{U}{2} \leq \mu \leq \frac{U}{2} = \Delta_2 = E_3 - E_2 \). In this interval of \( \mu \) the population numbers fulfill the condition

\[
N_{000} = N_{111} = N_{100} = N_{010} = N_{001} = 0. \tag{B13}
\]

Since the sum of all population numbers is equal to unity,

\[
1 = \langle \{ f_\nu, f_\nu^\dagger \} \rangle = \sum_\Gamma N_\Gamma, \tag{B14}
\]

and, also,

\[
N_{011} = N_{101} = N_{110}
\]

all three zero Fermion GFs,

\[
\begin{align*}
iF_{11}^0(i\omega) &= \frac{N_{110}}{i\omega + \frac{U}{2} + \mu} + \frac{N_{101}}{i\omega + \frac{3U}{2} + \mu} + \frac{N_{011}}{i\omega - \frac{U}{2} + \mu}, \\
iF_{22}^0(i\omega) &= \frac{N_{110}}{i\omega + \frac{U}{2} + \mu} + \frac{N_{011}}{i\omega + \frac{3U}{2} + \mu} + \frac{N_{101}}{i\omega - \frac{U}{2} + \mu}, \\
iF_{33}^0(i\omega) &= \frac{N_{101}}{i\omega + \frac{U}{2} + \mu} + \frac{N_{011}}{i\omega + \frac{3U}{2} + \mu} + \frac{N_{110}}{i\omega - \frac{U}{2} + \mu}, \tag{B17}
\end{align*}
\]

become equal to each other within the statistical description,

\[
\begin{align*}
iF_{11}^0(i\omega) &= iF_{22}^0(i\omega) = iF_{33}^0(i\omega) \\
&= \frac{2/3}{i\omega + \frac{U}{2} + \mu} + \frac{1/3}{i\omega - \frac{U}{2} + \mu}.
\end{align*} \tag{B18}
\]

As seen, when the chemical potential is within this interval of energy, 2/3 of the spectral weight of each orbital is concentrated at the energy \( \omega = -\frac{U}{2} - \mu \), while the rest of this weight is placed, by the sum rule, at \( \omega = \frac{U}{2} - \mu \).

From the Fermion GFs we find that the total spectral weight in the lower and upper poles is the same as within the single-electron picture,

\[
\begin{align*}
iF_{11}^0(i\omega) + iF_{22}^0(i\omega) + iF_{33}^0(i\omega) \\
&= 3 \cdot \left[ \frac{2/3}{i\omega + \frac{U}{2} + \mu} + \frac{1/3}{i\omega - \frac{U}{2} + \mu} \right] \\
&= \frac{2}{i\omega + \frac{U}{2} + \mu} + \frac{1}{i\omega - \frac{U}{2} + \mu}, \tag{B19}
\end{align*}
\]

and the same number of particles for the chemical potentials in this interval of energy

\[
n_d = n_1 + n_2 + n_3 \\
&= 3 \left[ \frac{2/3}{e^{\beta (-2U - \mu)}} + \frac{1/3}{e^{\beta (-3U/2 - \mu)}} + 1 \right] = 2. \tag{B20}
\]
This explains why the phenomenological recipe of the DFT LDA calculations with some fixed number of the localized electrons (in the case under consideration, two) works well: at large values of $U$ the contribution of the upper pole is not taken into account and when the states are degenerate, there is no difference, which of the orbitals of the non-filled shell that are occupied. However, it is instructive also to go further and consider the case when the degeneracy of these states is lifted away.

Let us imagine that some interaction pushes the energy of one of these orbitals below the other two (e.g. Hund rules, or long-range order). Then, we have to shift down the energy of, say, the first orbital, $\varepsilon_0^{(1)} \rightarrow \varepsilon_0 - \hbar \varepsilon_{eff}$, and, $\varepsilon_0^{(2)} \rightarrow \varepsilon_0$, $\varepsilon_0^{(3)} \rightarrow \varepsilon_0 + \hbar \varepsilon_{eff}$ in the Hamiltonian. The population numbers of the levels without electrons and with three electrons are still equal to zero because $\hbar \varepsilon_{eff} \ll U$. Although the energies of the three orbitals which share two electrons differ from each other by the magnitude $\hbar \varepsilon_{eff} \ll U$, at low enough temperatures $\beta^{-1} \ll \hbar \varepsilon_{eff}$ the population numbers become not equal to each other,

$$N_{110} = \frac{e^{\beta \hbar \varepsilon_{eff}}}{1 + e^{\beta \hbar \varepsilon_{eff}} + e^{-\beta \hbar \varepsilon_{eff}}} \approx 1,$$

$$N_{101} = \frac{1}{1 + e^{\beta \hbar \varepsilon_{eff}} + e^{-\beta \hbar \varepsilon_{eff}}} \approx 0,$$

$$N_{011} = \frac{e^{-\beta \hbar \varepsilon_{eff}}}{1 + e^{\beta \hbar \varepsilon_{eff}} + e^{-\beta \hbar \varepsilon_{eff}}} \approx 0,$$

(B21)

this leads immediately to a redistribution of the spectral weight

$$iF_{11}(i\omega) = \frac{N_{110}}{i\omega + \frac{1}{2} U + \mu} + \frac{N_{101}}{i\omega + \frac{1}{2} U + \hbar \varepsilon_{eff} + \mu} + \frac{N_{011}}{i\omega - \frac{1}{4} U + \mu} \approx \frac{1}{i\omega + \frac{1}{2} U + \mu},$$

(B22)

$$iF_{22}(i\omega) = \frac{N_{110}}{i\omega + \frac{1}{2} U + \mu} + \frac{N_{011}}{i\omega + \frac{1}{2} U + \mu} + \frac{N_{101}}{i\omega - \frac{1}{4} U + \mu} \approx \frac{1}{i\omega + \frac{1}{2} U + \mu},$$

(B23)

$$iF_{33}(i\omega) = \frac{N_{101}}{i\omega + \frac{1}{2} U + \mu} + \frac{N_{011}}{i\omega + \frac{1}{2} U - \hbar \varepsilon_{eff} + \mu} + \frac{N_{110}}{i\omega - \frac{1}{4} U + \mu} \approx \frac{1}{i\omega - \frac{1}{4} U + \mu},$$

(B24)

Thus, in this case, the spectral weight of the two localized orbitals is concentrated near the lower poles, $i\omega = E(110) - E(100) \approx -\frac{1}{2} U$, while the spectral weight of the third orbital is concentrated at the much higher energy, $i\omega \approx +\frac{1}{2} U$. This phenomenon is the orbital polarization, and it is caused here by the combined effect of the effective field and the sum rules. As we see, actually, the phenomenon of the orbital polarization is caused by two (in our case) different interactions which involve very different energy scales. First, the strong Coulomb intra-atomic repulsion compensates for the strong attraction of electrons by the nuclear potential to the extent, corresponding to the valence, displayed by the particular ion in the particular surrounding. The latter, should be taken into account via a Coulomb renormalization of the energies of the single-electron transitions and it is considered in the discussion and conclusion.

Second, a much smaller energy than the "Hubbard $U$" and Hund-rule integrals, like an energy of magnetic ordering, or, crystalline electric field, can provide a further polarization of the electronic shell. The Fermion GFs have purely single-electron form with location of orbitals at very different energies and, as we have seen, it is the intra-atomic interaction plus the sum rules for the many-electron spectral weights that provide their effectively single-electron form. Up to now we discussed only fully localized states.
Then, the system of equations for the GFs within the Hubbard-I approximation, atoms) and the transitions $\Delta$ under the Fermi level and contribute to the cohesive energy

$$H = (H_d^0 + H_d^U) + H_c^0 + H_{mix} + H_{hop};$$

$$H_c^0 = \sum_k \varepsilon_k c_k^\dagger c_k; \quad H_{hop} = \sum_{(ij)\nu} t_{ij}^\nu d_i^\dagger d_j^\nu;$$

$$H_{mix} = \sum_k V_k^\nu c_k^\dagger d_{1k} + V_k^\gamma d_{2k}^\dagger c_k.$$ 

Here we have chosen a simple form of the hopping, i.e. hopping is allowed from the orbital $\nu$ in one site to the same orbital in the neighboring ion, in a real lattice it is often not so.

The first immediate conclusion comes from the form of the Fermion GFs, $F$. Only a part of the $f(d)$-electron shell is delocalized since, at the energies $\omega \sim -\frac{1}{2}U$, the hopping matrix elements $t_{11}, t_{12}, t_{13}, t_{23}, t_{22}$ are exponentially small ($\psi_f \sim \exp (-\int dx \sqrt{2m}[U(x) - \Delta_1]$), where $U(x)$ is the potential separating the f-electrons belonging to neighboring atoms) and the transitions $\Delta_1 = E_2 - E_1 = -\frac{1}{2}U$ remain localized, while the $\Delta_2 = E_3 - E_2 = +\frac{1}{2}U$ may be located not very much higher the chemical potential and the magnitude of the hopping matrix elements $t_{33}$ may be noticeable; the mixing interaction is effective also only with the orbital which energy crosses a band. Then it looks like if we are back to the standard band picture, but only for the “upper” orbitals; therefore, the expected (index “$exp$”) equation for the Fermion GF for the third orbital is

$$F_{exp,33}^{-1}(i\omega) = [F_{33}(i\omega)]^{-1} - \frac{|V_k^{(\nu=3)}|^2}{i\omega - \varepsilon_k}, \quad (B25)$$

and the important physical consequence expected from this form is that the tails of this upper $f(d)$ band may go under the Fermi level and contribute to the cohesive energy\[3\]. Below we will see that this single-electron approach misses the important transfer of the spectral weight.

Let us consider the problem a bit more accurately. First we find the GFs for the transitions involved, the equations for the population numbers and, make conclusions about the spectral weights and the approximation needed to be done in order to make the problem as close as possible to the single-electron picture. First, since only the term $t_{33}(k)d_{1d}d_3$ is effective, the main role in the formation of the collective state will be played by those transitions for which the matrix elements $d_3^{2(\gamma\Gamma')} = \langle \gamma | d_3^{\Gamma'} \rangle$ is non-zero. It is convenient to introduce a short notation for them

$$2 \equiv [110, 111], \quad \bar{2} = [111, 110];$$

$$1 \equiv [100, 101], \quad \bar{1} = [101, 100];$$

$$1' \equiv [010, 011], \quad \bar{1}' = [011, 010]. \quad (B26)$$

Then, the system of equations for the GFs within the Hubbard-I approximation,

$$D_{HIA}^{-1} G_{HIA} = P, \quad (B27)$$

(which is sufficient for our target here) looks as follows

$$\begin{pmatrix}
\Omega_2 - \lambda_2 & \lambda_2 & \lambda_2 \\
\lambda_1 & \Omega_1 - \lambda_1 & -\lambda_1 \\
-\lambda_1 & \Omega_1' - \lambda_1' & \\
\end{pmatrix}
\begin{pmatrix}
G^{22} & G^{21} & G^{2i'} \\
G^{12} & G^{11} & G^{1i'} \\
G^{12'} & G^{1i2'} & G^{1i'} \\
\end{pmatrix}
= \begin{pmatrix}
P^{22} & 0 & 0 \\
0 & P^{11} & 0 \\
0 & 0 & P^{1i'1'} \end{pmatrix}. \quad (B28)$$

Here we have used the notations for transitions 2, 1, 1’ used above (don’t confuse with the orbital numbers): $G^{22} = -i\langle T X^2 X^2 \rangle_{i\omega} \equiv -i\langle T X^{[110,111]} X^{[111,110]} \rangle_{i\omega}$, etc.

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\[ \Omega_j = i\omega - \Delta_j; \quad \lambda_j \equiv \lambda(k, i\omega) \]
\[ P_j = \left[ t_{33}(k) + \frac{|V(k)|^2}{i\omega - \varepsilon_k} \right] P_j, \quad j = 2, 1', \quad (B29) \]
\[ P_j \equiv P^{ij}; \quad P_2 = N_{111} + N_{101}; \]
\[ P_1 = N_{100} + N_{101} \approx N_{101}; \]
\[ P_{1'} = N_{010} + N_{011} \approx N_{011}. \quad (B30) \]

Then,
\[ \mathbf{G}_{HIA} = \frac{1}{||D_{HIA}^{-1}||} \begin{pmatrix} \Phi_{11'}P_1 - \lambda_2 \Omega_{1'}P_1 & -\lambda_2 \Omega_1P_1' \\ -\lambda_1 \Omega_1P_2 & \Phi_{21'}P_1' \end{pmatrix} \]
\[ \lambda_1 \Omega_2P_1' \]
\[ (B31) \]

\[ ||D_{HIA}^{-1}|| = \lambda_2 \Omega_1 \Omega_{1'} - \lambda_2 \Omega_1 \Omega_{1'} - \lambda_2 \Omega_1 \Omega_{1'} - \lambda_2 \Omega_1 \lambda_{1'}, \]
\[ \Phi_{ij} = \Omega_1 \Omega_j - \Omega_1 \lambda_j - \lambda_1 \Omega_j. \quad (B32) \]

Let us write down the Fermion GFs via the Hubbard GFs. We start with the Fermion GF of the delocalized "orbital"
\[ F_{11'}^{HIA} = d_i^\dagger(d_{1'}^\dagger)^b G^{ab} \]
\[ = G^{22} - G^{21} - G^{21'} + G^{12} + G^{11'} + G^{11} + G^{11'} \]
= \[ \Omega_2 \Omega_1 \Omega_{1'} - \lambda_2 \Omega_1 \Omega_{1'} - \Omega_2 \lambda_1 \Omega_{1'} - \Omega_2 \Omega_1 \lambda_{1'}. \quad (B33) \]

and inspect the form of this GF in two regions of energy, \( i\omega \sim \Delta_2 \) and \( i\omega \sim \Delta_1 \). In order to see a rough structure, let use the fact that the magnitude of the effective field, \( \hbar_{eff} \), is invisible on the scale of energies \( \sim U \), therefore, we can put \( \Omega_1 = \Omega_{1'} \); and
\[ P_2 + P_1 + P_{1'} = (N_{110} + N_{111}) + N_{101} + N_{011} = 1, \quad (B34) \]
(with the accuracy \( N_{100} = N_{010} = N_{001} \approx 0 \)); then, we see that the approximate GF for the third orbital is:
\[ F_{11'}^{HIA} = \frac{P_2 \Omega_1 + (1 - P_2) \Omega_2}{\Omega_2 \Omega_1 - \lambda(1 - P_2) \Omega_2 - \lambda P_2 \Omega_1}. \quad (B35) \]

Then, we have a third-order equation for the spectrum. In order to make the further formulas readable we switch off the mixing since this does not change the principal features of the model. From the poles of this GF we find the band spectrum:
\[ E^{\pm}_k = \frac{1}{2}(\lambda_k + \nu_k); \quad \nu_k = \sqrt{(U + \lambda_k)^2 - 4\lambda_k U(1 - P_1)}. \quad (B36) \]

This formally coincides with the spectrum of the s-band Hubbard model in the Hubbard-I approximation if we take into account that, in the form of the spectrum, we used the choice \( \varepsilon_0 = -3U/2 \) explicitly. The GF of the delocalized orbital can be written then in the form:
\[ F_{11'}^{HIA} = \frac{u_k^2}{\omega - E_k^+} + \frac{v_k^2}{\omega - E_k^-}, \quad (B37) \]
\[ \text{where} \]
\[ u_k^2 = \frac{1}{2} \left( 1 - \frac{\lambda_k - U(1 - 2P_2)}{\nu_k} \right), \quad v_k^2 = 1 - u_k^2. \quad (B38) \]

Now we have a look at \( F_{22} \) and \( F_{33} \). Since \( t_{2u} = V_{2u} = 0 \), and the matrix elements \( d_i^\dagger \) in the expansion
\[ \mathbf{F}_{11}^{HIA} = d_i^\dagger(d_{1'}^\dagger)^b G^{ab} \quad (B39) \]
are equal to zero for the transitions \( a = 2 \equiv [110, 111]; 1 \equiv [100, 101]; 1' \equiv [010, 011] \). Therefore,

\[
F_{22}^{HIA} = \frac{N_{110} + N_{101}}{i\omega + U/2 + h_{e,f}} + \frac{N_{011} + N_{111}}{i\omega - U/2 + h_{e,f}},
\]

\[
F_{11}^{HIA} = \frac{N_{110} + N_{011}}{i\omega + U/2} + \frac{N_{101} + N_{111}}{i\omega - U/2},
\]

i.e. the only difference with the case when the hopping and mixing are absent is that the population number \( N_{111} \neq 0 \). Indeed, we find from from the GF \( G^{11} \):

\[
N_{111} = (N_{111} + N_{110}) \sum_k |a_k^2 f(E_k - \mu) + b_k^2 f(E_k + \mu)| \equiv (N_{111} + N_{110}) \Theta \neq 0.
\]

(B42)

(B43)

Here,

\[
a_k^2 = \frac{1}{2} \left[ 1 - \frac{U + \nu_k - 2\nu_k(1 - P_2)}{\nu_k} \right], \quad b_k^2 = 1 - a_k^2.
\]

(B44)

We consider the situation when the bottom of the conduction band is above the energy of the lower transitions, \( \lambda_{k,atom} > \Delta_1, \Delta_2 \), and the energy of the upper transition is above the Fermi energy, \( \Delta_2 > \varepsilon_F \). Since the level \( \Delta_2 = U/2 \) before switching hopping and mixing was empty, the band \( \lambda_k \), being transformed into \( E_k \), changing is filled only slightly and, therefore, \( \Theta \ll 1 \). Within the accuracy we need this makes it sufficient to replace the sum \( \Theta(P) \) by \( \Theta(P^{(0)}) \), i.e. to find it without self-consistency, using non-perturbed values for the population numbers. Then, \( \Theta \) becomes just a given small number (which value we do not need to know here). Therefore, although the analytical form of the GFs, \( F_{22}^{HIA}, F_{11}^{HIA} \), coincides with the \( F_{22}^{00}, F_{11}^{01} \), but the population numbers in the numerators, which determine the spectral weights, are slightly redistributed. Since a further analysis is possible only numerically, in order to get some impression of what is changed let us formally write down the population numbers in terms of \( \Theta \) using the sum rule for the population numbers and the GFs \( G^{011111}, G^{1011111111}, G^{1101111111110} \):

\[
N_{111} = \frac{\Theta}{1 + \Theta|e_1 + e_2|}, \quad N_{110} = \frac{1 - \Theta}{1 + \Theta|e_1 + e_2|},
\]

\[
N_{011} = \frac{\Theta e_1}{1 + \Theta|e_1 + e_2|}, \quad N_{101} = \frac{1 - \Theta e_2}{1 + \Theta|e_1 + e_2|},
\]

\[
e^{\beta(U/2 - \varepsilon_F)} e_1 = e^{\beta(U/2 - \varepsilon_F)} e_2 = e^{\beta(U/2 - \mu)}.
\]

(B45)

Since at \( \lambda_k = 0 \) we have that \( P_2 = P_2^{(0)} = N_{111}^0 + N_{110}^0 = N_{110}^0 \) and equal to unity when the degeneracy is removed, it is clear that \( (1 - P_2) \ll 1 \). Using this, we can write down an approximate expression for the Fermion GF,

\[
F_{33}^{HIA} \approx \frac{1 - P_2}{\omega + \frac{U}{2} + (1 - P_2)\lambda_k} + \frac{P_2}{\omega - \frac{U}{2} + \lambda_k P_2}.
\]

(B46)

We can neglect a weak and non-important dispersion \( \propto (1 - P_2)\lambda_k \) in the lower pole since this Hubbard sub band is fully filled and does not contribute to the cohesive energy of the system. However, the important thing following from this expression is that due to the delocalization of the orbital in the region of energies \( \omega \sim \frac{U}{2} \) the bandwidth of the band decreases, the spectral weight in upper pole is also decreasing from unity to \( P_2 < 1 \), and in a lower pole a small, but non-zero weight arises.

Thus, we see that the function \( F_{11'} \) is reduced indeed to the form of \( F_{exp11'} \) only in the case when \( P_2 = N_{110} + N_{111} = 1 \). Since all other population numbers are not equal to zero, \( P_2 < 1 \) and the picture based on an effective single-electron potential should be corrected.

Switching on mixing does not change the picture in this approximation, but slightly Shifts the value of \( \Theta \) and \( P_2 \). What physical consequence can be expected of those shifts of the spectral weights?

First, since a non-zero spectral weight of the orbitals 1 and 2 has appeared at the energy \( i\omega \sim U/2 \), and the energetic barrier between the neighboring ions is not that wide nothing prevents a hopping between these orbitals belonging to different ions to develop, as well as mixing of these orbitals with the conduction bands. Therefore, the self-consistency loops should lead to the formation of bands due to hopping, etc. It should be noted, that the magnitude of the
shifted spectral weight is small because its value is determined by the competition between the Hund-rule intratomic exchange energy and cohesive energy due to a delocalization of the empty part of the $t_{1g}$-orbitals. The latter essentially depends on the degree of proximity of the upper transition $\Delta_2$ to the Fermi energy $\bar{\epsilon}$ and, as will be seen below, the Hund-rule integrals split the upper transitions. This also leads to a suppression of the band formation with the transitions which are much above Fermi energy.

Second, the expectation that pure Fermion bands will be developed from the "upper" orbitals happen to be valid within the approximation $N_{111} = 0$. Actually, there is no purely single-electron bands.

Third, these bands are narrowed by the spectral weights. Although this is a well known effect from the studies of the Hubbard models, this is important in our discussion of an possible improvement of the ab initio calculations: even when SIC mimics the orbital polarization and improves essentially the description of the matter, it does not provide a fully correct physical picture.

Fourth, not only the bandwidth of the band $t_{1G'}(k)$ is decreased, $t_{1G'}(k) \Rightarrow t_{1G'}(k)[N_{110} + N_{111}]$, but, also, a part of the spectral weight is moved from the high-energy region $i\omega \sim \Delta_2$ to the low-energy $i\omega \sim \Delta_1$ (see the Eqs for the Fermionic GF's $F$). Since usually the main contribution to the value of the moment comes from the localized orbitals, one can expect a slight deviation (decrease) of this moment from an integer value. In rare earths this effect is weak, but it is clear that, for example, in compounds with intermediate valence the deviation of the moment from integer is quite strong. Thus, this effect of the transfer of the spectral weight occurs due to delocalization of one of the transitions (detailed consideration of the mechanism of delocalization due to a correlation-caused transfer of spectral weight is given in a recent paper[2]).

Fifth, when a long-range magnetic order arises in the system, the effective field, shifting the lower levels, as discussed above, changes the magnitudes of all population numbers (again due to the sum rule); the latter may change the bandwidth. Thus, if the correlated bands are involved into the formation of magnetism, the essential physics of the formation of the magnetic moment consists not in a rigid (self-consistent) shift of the bands, but in the changes of the bandwidths involved. From the technical point of view the lesson which one can extract from the consideration of this model is the following. The speculations, based on Equations (B22) and (B24) and which lead us to the Eq. (B25) might be considered as a ground for the ab initio calculations either within the standard model for the lanthanides and, also, within the SIC method, where SIC is applied to some of the orbitals. Some of the orbitals are fully localized and are placed very deep in energy either "by hands" in first case, or by a SIC potential in the second one, while only the orbitals remaining at higher energies are delocalized. However, as we see from Eq. (B40) this picture is not fully correct it misses the shifts of the spectral weights. As we shall see below, a very simple recipe to correct for this exists. In spite of the simplicity of the approximation, Hubbard-I, used in this example (which is the same in spirit as the ARF, discussed in the previous section), should reflect the mechanisms of the spectral weight transfer correctly since the driving mechanism is the sum rules, which comes from the exact commutation relations. Therefore, the mechanisms discussed above are expected to remain valid in higher approximations.

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FIG. 1. The first contribution to the GF comes from the hopping/mixing matrix element. The solid line is the locator, \( D \), the circle is the spectral weights and the wavy line is the hopping/mixing. All lines in further graphs can be renormalized by this insertion.

FIG. 2. The second diagram, a, appearing in SCPT, The dashed line is the Coulomb interaction.

FIG. 3. The exchange graph, b, corresponding to the expression given in Eq.(56).

FIG. 4. A loop diagram in SCPT, graph c. The zig-zagged line represents the end in \( \epsilon \), the constants of the algebra. The thick line represents the incoming and outgoing indices in \( \epsilon \), i.e. \( 1^\prime \) and \( 2 \) in \( \epsilon_4^2 \). The corresponding analytical expression is given by Eq.(67).

FIG. 5. Contribution d in Eq.(68). The curly line represents the Bosonic Green function \( \langle T Z^{6_b} Z^{4_b} \rangle \).

FIG. 6. Contribution e in Eq.(69).

FIG. 7. Contribution f in Eq.(70).

FIG. 8. Graph which has an exact analogy in WCPT. A two-exchange process. Contribution g.

FIG. 9. Graphs which has an exact analogy in WCPT. Contribution h.

FIG. 10. Graphs which has an exact analogy in WCPT. Contribution k.

FIG. 11. Graph which has an exact analogy in WCPT. An exchange diagram with a loop insertion. Contribution l.

FIG. 12. Graph which has an exact analogy in WCPT. An exchange diagram with two loop insertion. Contribution m.

FIG. 13. Graph with one line renormalized by the first correction, Fig. 3. Any locator line can be dressed by the graph in Fig. 3. Contribution n.

FIG. 14. The screening process, the localized transitions are screened by the delocalized transitions. The screening of the delocalized transitions by localized is very weak due to the large energy gap involved.
FIG. 15. The screening process can be continued, however, only delocalized transitions screen the Coulomb interaction.