Theory of strongly correlated electron systems.

I. Exact Hamiltonian, Hubbard-Anderson models and perturbation theory near atomic limit within non-orthogonal basis set

Igor Sandalov\textsuperscript{1,2}, Börje Johansson\textsuperscript{1}, Olle Eriksson\textsuperscript{1}

\textsuperscript{1}Condensed Matter Theory Group, Institute of Physics, Uppsala University, Box 530, SE-751 21 Uppsala, Sweden,

\textsuperscript{2}Dept. of Physics, Linköping University, SE-581 83 Linköping, Sweden

(March 21, 2022)

Abstract

The theory of correlated electron systems is formulated in a form which allows to use as a reference point an \textit{ab initio} band structure theory (AIBST). The theory is constructed in two steps. As a first step the total Hamiltonian is transformed into a correlated form. In order to elucidate the microscopical origin of the parameters of the periodical Hubbard-Anderson model (PHAM) the terms of the full Hamiltonian which have the operator structure of PHAM are separated. It is found that the matrix element of mixing interaction includes ion-configuration and number-of-particles dependent contributions from the Coulomb interaction. In a second step the diagram technique (DT) is developed by means of generalization of the Baym-Kadanoff method for correlated systems. The advantages of the method are that i) a non-orthogonal basis can be used, particularly, the one which is generated by AIBST; ii) the equations for Green’s functions (GFs) for the Fermi- and Bose-type of quasi-particles can be formulated in the form of closed system of functional
equations. The latter allows to resolve some difficulties of previous versions of the DT. Although the expressions for all interactions depend on the overlap matrix, it is shown that the theory is formally equivalent to one with orthogonal states with redefined interactions. When the PHAM is treated from the atomic-limit side the vertexes are generated by kinematic interactions. The latter arise due to non-trivial commutation relations between $X$-operators and come from the mixing, hopping and the overlap of states. The equations for GFs are derived in different approximations for vertexes, corresponding to the Hubbard-I, mean field, and random phase approximations, respectively. The technique is also extended to the case of intersite Coulomb interaction. The self-consistent equation for "Hubbard $U$-s" is derived. Both interactions, kinematic mixing and hopping, and Coulomb interaction of $f$- and non-$f$-electrons contribute to the screening of bare $U$. The diagram techniques for pure Hubbard, Anderson models, $s$ – $f$-model and for iso- and anisotropic spin Hamiltonians can be obtained from the developed approach as special cases.

71.25.-d, 71.25.+x, 71.27.+a, 71.28.+d
I. INTRODUCTION

The calculations of properties of real materials in the language of many-body wave functions are incomparably more effort- and time-consuming than the ones based on the density functional theory (DFT). However, DFT is designed for calculation of ground-state properties and, by construction, is expected to have limited use if one is interested in dynamic properties. The only available regular way to calculate quasiparticle properties is to make use of some diagram technique. The latter usually involves expressions for secondary quantization. Therefore, anyhow one needs some single-electron equation which would generate a set of wave functions with proper boundary conditions. The DFT-based ab initio band structure calculations (AIBST) seems to be a reasonable starting point at least for the conduction electrons. Therefore, the corresponding Schrödinger equation can be used as the one which generates a convenient basis set of wave functions for formulation of secondary quantized Hamiltonian. On the other hand it is far from obvious how DFT can be used for correlated electrons. Materials which usually are classified as systems with strong electron correlations (SEC) show wide spread properties such as magnets with localized and partly localized moments, Mott insulators, Kondo lattices, heavy fermion systems, and high-$T_c$ superconductors. These materials contain elements with an open $d$- or $f$-shell which often are main source of difficulties in a theoretical description both within the local spin density approximation (LSDA) and model approaches. The classical example of a ground state property which the LDA approach is not able to describe is the Mott insulating state where materials with odd number of electrons per primitive cell are insulators. The special features which arise in these systems due to SEC are configuration-dependent mixing and hopping (see ref.3) and the hybridization-dependent spectral weight transfer. Even much simpler properties as the atomic-like Hund’s rules are not reproduced within DFT. The common way to correct the situation in AIBST is to use phenomenological methods like the self-interaction correction (SIC), and the so-called LDA+U method of Brandow. These methods provide a picture close to the discussed one by Brandow in the Hartree-
Fock approximation: the SIC corrected orbitals (selected at the onset of the calculation) are pushed down by the SIC potential, usually to 8-11 eV below Fermi energy, \( \epsilon_F \), while all other \( f(d) \)-orbitals remain above \( \epsilon_F \) and are empty. From the point of view of phenomenological theories of SCES, like the periodical Anderson model (PAM), the picture generated by SIC is not satisfactory since usually mixing interaction disappears when \( f(d) \)-level is below the bottom of conduction band. This makes it impossible to check the PAM mechanisms within AIBST. The LDA+U method gives a much smoother picture, since the values of the Hubbard \( U \) are taken to be 2-6 eV. The models used are also different and there is no clear arguments why in one case should us the Hubbard model (i.e. mixing is equal to zero) whereas another case the PAM (i.e. hopping is neglected). This raises the question whether these arguments can be derived from strict microscopical approach or not as well as whether some minimal model can be derived from the exact full Hamiltonian or not. Below we will show that when the system contains a subsystem with (quasi)localized electrons, the full Hamiltonian \( H \) always contains a part, which corresponds to the periodical Hubbard-Anderson model (PHAM). Then, representing \( H \) in the form \( H = H_{PHAM} + H' \) we will construct a diagram technique which will make possible both calculation of renormalization of \( H_{PHAM} \) by remaining Coulomb terms from \( H' \), and to understand to what extent picture obtained within the PHAM is accurate.

Another problem, which is difficult to tackle within the AIBST, is to calculate the spectrum of quasi-particles. Although there are no grounds to consider the eigenvalues of Kohn-Sham equations as energies of quasi-particles, this is quite common practice due to its relative simplicity. For some cases a simple formula which connects these energies can be written. Part of the dispersion and life-time of quasi-particles, nevertheless, seem to be lost. However, the DFT potential treated as a self-energy by construction can neither provide the energy dependence of the real part of the self-energy, nor reflect the scattering of quasi-particles, since it does not have imaginary part. This is especially important for the case of SEC, where \( \Sigma_{k\lambda}(E) \) sometimes can give three solutions of the equation for the quasiparticle energy \( E = \epsilon_{k\lambda} + R\text{e}\Sigma_{k\lambda}(E) \) (e.g., satellites in the photoelectron spectra of \( Ni \)
while the DFT potential, $v_{DFT}$, due to absence of a dependence on energy can provide only one solution to this equation. Thus, in order to obtain information about these properties of the system one needs a many-body theory. In the present paper we intend to develop an approach for the systems with $f(d)$-electrons in the strong-coupling regime, therefore, we choose perturbation theory from the atomic limit. As follows from the above argument it is desirable to start with self-consistent AIBST where the localized electrons are treated as core electrons. Here we will treat these localized (or almost localized), electrons with the help of Hubbard operators $X^{pq} \equiv |p\rangle\langle q|$. The latter describe transitions from the state $p$ of the ion to the state $q$. The first step then is a formulation of the Hamiltonian of the system in terms of these variables. In the case of rare earth metals (Russel-Saunders coupling) and a model of homogeneous gas for conduction electrons the work by Irkhin and Irkhin can be of great help. Particularly, a way to construct many-electron secondary-quantized operators, which describe creation and destruction of the $f$-ion states with the help of the standard technique used in atomic spectroscopy, is thoroughly described therein. This technique has been also successfully used for derivation of the form of $f$-density for use in DFT-based AIBST. The case of $j-j$-coupling is developed much less since an accurate account of effects of non-local exchange interaction should be performed within a fully relativistic field-theory (the case of strong spin-orbit coupling); the cases when a relativistic effects can be taken into account via perturbative Hamiltonian, can be treated within our approach too. There is one more important motivation for a microscopical derivation of the correlated form of Hamiltonians and an effective Hamiltonians. An extension of AIBST to thermodynamics is based usually on mapping of the constrained AIBST to some model; the parameters of the model are calculated from fitting the model’s energy surface to the DFT one for some selected configurations of the system. Obviously, the choice of the model is not unique, i.e., for sufficiently large number of parameters many different models can reproduce the DFT-derived dependence of energy on the parameters involved. Besides, being within framework of density functional formalism it is very difficult to avoid classical approximations, that can introduce uncontrolled errors. Below we shall show that such
derivation can be performed for arbitrary localized set of orbitals. This means that the parameters of the model, as well as correcting terms, are representation-dependent. Probably, the best starting step is a DFT-AIBST. As will be seen, our approach for derivation of the correlated form of Hamiltonian in the particular case of Russel-Saunders coupling is not fully identical to the one, suggested by Irkhin\cite{21}, but their main results can easily be used for our purposes. The formalism will be developed in general notations, so that different cases can be considered. Compared to the approach developed in Ref.\cite{21} the present paper the main emphasis will be put on the next logic step of development of the theory, namely, on the derivation of a regular diagram technique from atomic limit for the evaluation of Green’s functions within the basis chosen.

The fact, that SEC have local, site-centered nature dictates a requirement of the approach: the strong on-site Coulomb interactions should be taken into account first. This can be done much easier within the representation of some site-centered wave functions. Then the question arises immediately: should one first orthogonalize the wave functions centered on different atoms and then take into account correlations or, vice versa, first to take into account local interactions and then treat somehow non-orthogonality? The answer, of course, depends on the ratio of the bandwidth, generated not only by non-orthogonality, but by all possible mechanisms (due to self-consistency) and the largest matrix element of local Coulomb interaction. It is clear that a big enough Coulomb interaction can cause strong shift of the levels of orbitals, that, in turn, can strongly change the overlap with neighboring atoms. This picture has been many times confirmed by the calculations, which use LDA+U-, SIC (self-interaction correction), or Hartree-Fock approximation: the orbital, which was delocalized before application of, say, SIC, becomes completely localized after applying SIC, loosing simultaneously all mixing and overlap with neighbors. Thus, for such materials the answer seems to be clear and conceptually important: first should be taken into account SEC and only after that the overlap, mixing and hopping should be treated. Strictly speaking, the final band structure should not depend on our choice of perturbation theory: from atomic or itinerant limit we develop perturbation theory. In the latter case a
necessity arises to generalize the three-body Faddeev equations\(^2\) to the \(n\)-body ones and to work with many-electron GFs. Although this is not done yet, one can expect that an analysis of the contributions from the closed channels of scattering should raise the same problems, which we have deal with when start from the atomic limit. Returning to our approach, we immediately find that the non-orthogonality of orbitals causes a problem: a regular diagrammatic approach for the description of correlations of electrons in open many-electron inraatomic shells, for the case when the system is near the atomic limit and the basis used is non-orthogonal, has not been developed yet. We have not found a method that allows to treat the non-orthogonality within the versions of the DT, developed by Kuramoto\(^2\) and Grewe\(^3\), as well as for other version of the DT, that has been developed by Westwansky and Pawlikowski\(^2\) and by Zaitsev\(^2\) (WPZ) for the \(s\)-band Hubbard model (the group \(SU(4)\)).

The problem is that in the case of a non-orthogonal basis the picture of interaction cannot be used since we are not able to calculate the time dependence of the conduction-electron operators \(c_{\kappa\lambda}(t)\) and of the \(X_n(t)\)-operators even for the zero Hamiltonian (18): \(c(t)\) and \(X(t)\) are coupled by the overlap matrix. In the WPZ-technique one more open question exists. Namely, as has been shown\(^2\), compared to the conventional DT for fermions and bosons, the set of diagrams in the DT for the \(s\)-band Hubbard model is not unique, being dependent on the order in which different \(X\)-operators are picked up from the chronologically ordered product \(\langle T\{X_1(\tau_1)\ldots X_m(\tau)\ldots X_n(\tau_n)\}\rangle\) for Wick’s decoupling. In order to avoid under- or double counting, this way of the formulation of the DT must be complemented by a system of priority, or hierarchy, for the \(X\)-operators. The recipe for the \(s\)-band Hubbard model is developed. However, it is difficult to use this recipe in practical calculations for the \(d\)- and \(f\)-systems due to very large number of the electron transitions involved (this number quickly grows with the number of electrons in the shell). Another important moment is connected with existence of closed system of equations for GFs. The latter give us an opportunity to introduce the accurate definitions for self-energy and vertexes. We shall show below that an absence of such definitions in earlier theories can lead to erroneous results. As will be seen, the mentioned difficulties can be resolved by making use of a properly generalized method
of Baym and Kadanoff where the diagram technique can be constructed via equations of motion. Within this technique the hierarchy is automatically established by the choice of the variables, Grassman or boson ones, which are used in the Hamiltonian of external fields.

The aims of the present paper can be formulated as follows:

1) To derive an approximate Hamiltonian in a local many-electron representation, which allows to use as a reference point the LDA Hamiltonian, $H_{LDA}$, for a description of delocalized electrons, but the many-electron description of the localized or, almost localized, electrons. To separate from the total Hamiltonian the one corresponding to the generalized Hubbard-Anderson model in order to elucidate the microscopical origin of the parameters of this model. 2) To derive a closed system of equations for the Green’s functions and to develop a diagram technique, that allows one to work with a non-orthogonal basis set which is free from the problem of a hierarchy between Hubbard operators.

3) To derive a few ”common” approximations for the case of a generalized Hubbard-Anderson model within a non-orthogonal basis. Particularly, to derive the self-consistent equations for the set of ”Hubbard U-s.

4) To inspect the role of remaining terms of the Coulomb Hamiltonian in formation of the Hubbard-Anderson model and to make an attempt to formulate ”minimal” model, which describes formation of the low-energy physics in the SEC system.

5) We will finally compare our equations with some of available results of other authors.

It is worth noting that i) although our derivation of perturbation theory is based on the ideas similar to ones used by Ruckenstein and Schmitt-Rink (Schwinger’s source theory) the resulting Green’s function technique is closer to the one used by Zaitsev and Izyumov et al. (within ”boson” hierarchy) since we are using local Green’s functions as a zero-order limit instead of the itinerant limit used in ref. 24; ii) we suggest to use the self-consistent LDA potential for generating the set of wave functions and eigenvalues as a convenient first step, taking in a proper way symmetry and detailed charge distribution of the material of interest, but not the conceptional framework of the density functional theory (DFT). We emphasize that we will use a more or less standard many-body approach, which is different
from DFT ideology: in our case the expressions for the ground state energy, free energy and excitations should be found directly from the calculated GFs.

The content of the next sections is the following. In Sec.IIA, assuming that the self-consistent solution of the band problem within LDA or some other convenient potential with the \( f(d) \)-electrons treated as core is found, we use a local set of site-centered non-orthogonal functions for a transformation of the total Hamiltonian to a form that is convenient for our further purposes with representation of non-orthogonal field operators. Then we show that the Green’s function, defined on these non-orthogonal operators, reproduces the LDA problem. In section IIB we introduce the many-electron representation and we derive the generalized Hubbard-Anderson model corresponding to the secular equation of the LDA problem plus those terms of Coulomb interaction which are responsible for formation of the \( f(d) \)/shell of the ion.

Sec.III is devoted to the diagram technique itself. We start with a derivation of commutation relations between many-electron operators of the \( f \)-shell and delocalized electrons. Then with the help of these relations the equations of motion for the operators of quasi-fermion and quasi-boson intra-atomic transitions are derived. The latter equations allow us to find out what type of Schwinger’s sources should be introduced into the theory and to derive a closed system of equations for Green’s functions (GFs) in terms of functional derivatives of generating functional.

In Sec.IV we rewrite the theory in a more compact form, introducing the self-energies and vertexes, and derive a few approximations. The equation for the self-energy is written here in terms of functional derivatives, which is convenient for iterations. After that the equations for GFs within the ”Hubbard-I” approximation are formulated. This approximation corresponds to the vertex equal to zero. Next approximations require knowledge of the vertex. Therefore, we formulate the equation for the self-energy in terms of the vertex. This allows us to derive a mean field theory, beyond the Hubbard-I approximation, in which the energies of \( f \)-transitions are self-consistently renormalized by kinematic interactions caused by mixing interaction and hopping. The abovementioned self-consistent equation for Hub-
bard $U$-$s$ is composed of these equations. At last, by making use of transformation to a
description in terms of an effective field, we formulate the equations for the "random phase
approximation" (RPA), which describe the self-dressing of kinematic interactions.

In Sec. V we consider some of remaining terms of Coulomb interaction. The purpose of
this section is two-fold: i) to generalize the equations and method for the case of Coulomb
interaction; ii) to discuss the correction from Coulomb interaction of $f$-electrons and conduc-
tion electrons to the self-consistent equation for "Hubbard $U$-$s$". The paper is completed by
Sec.VI where discussions and conclusions are given. Applications of the presented technique
to concrete problems will be given in forthcoming papers.\[20\]

II. HAMILTONIAN AND THE HUBBARD-ANDERSON MODEL

A. Non-orthogonal representation

In order to have a possibility to correct the band structure and the ground state prop-
ties, obtained by the LDA calculation in a regular way we first introduce the exact Hamil-
tonian of the system in second quantization using some complete set of wave functions, for
example, plane waves. One can expect that the many-body corrections to the spectrum and
wave functions of conduction electrons will be small\[34,35\], which motivates to start evalua-
tions with the LDA Hamiltonian. We note, however, that the construction described below
allows to start from any convenient single-electron potential (e.g. a self-interaction corrected
one). Let us separate the LDA part of full Hamiltonian and develop a many-particle per-
turbation theory for the Green’s functions over the deviation between the exact and LDA
Hamiltonians.

The corrections which we are going to discuss come mainly from on-site-localized
Coulomb repulsion in the open $d$- or $f$-shell. From a technical point of view a serious
disadvantage of local representation is the non-orthogonality of wave functions, centered
on different sites. The corresponding diagram technique should necessarily include over-
lap matrices. The same reason, however, turns out to be an advantage since it allows to easily separate the on-site interactions from the contributions coming from other sites. In the present paper we restrict ourselves with a non-relativistic consideration, i.e., the total Hamiltonian of the system we shall start with is:

$$H = (T + H_{en}) + H_{ee} + H_{nn} = \sum_\sigma \int dr \psi_\sigma^\dagger(r) \left( \frac{p^2}{2m} - \sum_j \frac{Z_j e^2}{|r - R_j|} \right) \psi_\sigma(r) + \frac{1}{2} \sum_\sigma \sum_\sigma' \int dr \int dr' \psi_\sigma^\dagger(r) \psi_\sigma^\dagger(r') \frac{e^2}{|r - r'|} \psi_\sigma'(r') \psi_\sigma(r) + \frac{1}{2} \sum_j \sum_{j' \neq j} \frac{Z_j Z_{j'} e^2}{|R_j - R_{j'}|},$$

where the first term includes the kinetic energy and the electron-nuclei interaction, the second term the electron-electron interaction and the last term the nucleus-nucleus interaction. It should be emphasized that the electron operators $\psi_\sigma(r)$ are constructed from some complete set of functions and, therefore, the field operator $\psi$ and, correspondently, Hamiltonian $H$, are exact. Let us now introduce the set of wave functions, $\phi_{k\lambda}(r)$, which are the solution to the LDA band problem:

$$\left[ \frac{p^2}{2m} + v_{LDA}(r) \right] \phi_{k\lambda}(r) = \epsilon_{k\lambda} \phi_{k\lambda}(r),$$

where $v_{LDA}(r)$ is the LDA effective potential, $\epsilon_{k\lambda}$ the Kohn-Sham eigenvalue, and $\lambda$ is a band index. We will use below the solutions of this equation only as an almost complete set, on the one hand, in order to reformulate our full problem into convenient for our aims representation, and in order to express the energies of conduction-electron quasi-particles in terms of the Kohn-Sham eigenvalues, on the other hand. Since the set $\phi_{k\lambda}(r)$ is orthonormalized, corresponding annihilation operators can be obtained simply by projection from the full field operator, $\hat{a}_{k\lambda\sigma} = \int dr \phi_{k\lambda}^* (r) \hat{\psi}_\sigma(r)$. Next, we separate the full field operator into two parts,

$$\psi_\sigma(r) = \psi_\sigma^{(LDA)}(r) + (\psi_\sigma(r) - \psi_\sigma^{(LDA)}(r)) = \psi_{1\sigma}(r) + \psi_{2\sigma}(r),$$

where
\[\psi_{1\sigma}(r) = \psi^{(LDA)}_{\sigma}(r) = \sum_{k\lambda} \phi_{k\lambda}(r) a_{k\lambda}.\] (4)

Let us now insert \(\psi = \psi_1 + \psi_2\) into the exact Hamiltonian (1), and of all terms which arise we take into account only the ones which contain only \(\psi_1\). We stress that the approximation made here should be kept in mind, since for a description of some experiments, for instance the ones involving large-energy perturbation, (e.g. photoelectron spectroscopies) this set may be insufficient. For these cases a consideration within this reduced Hamiltonian would miss essential physics of the phenomena (essential additional terms in the Hamiltonian).

The obvious, strict way to construct the standard weak-coupling perturbation theory which takes into account the effects of Hubbard \(U\) and starts from \(H_{LDA}\) as the zero Hamiltonian is to represent \(H\) in the form:

\[H = (T + H_{en} + V_{LDA}) + H_{nn} + (H_{ee} - V_{LDA}) = H_0 + H_{int} = H_0 + H_{int}.\] (5)

It worth noting that although we use \(V_{LDA}\) one can start with any convenient potential. This opportunity may be especially important for consideration of problems with constrained boundary conditions (like, for example. quantum dots). In consideration below we will work, however, with the approximate Hamiltonian, having neglected all the \(\psi_2\)-dependent terms:

\[H = \int dr \psi_{1\sigma}^\dagger(r) \left( \frac{p^2}{2m} + v_{LDA}(r) \right) \psi_{1\sigma}(r) + \left( H_{nn} + H_{ne} + H_{ee} - \int dr \psi_{1\sigma}^\dagger(r)v_{LDA}(r)\psi_{1\sigma}(r) \right),\] (6)

with conventional notations.

The further steps are the following. The first one is to construct expansion of field operators in the formalism of secondary quantization in such a way that the equation of motion for the Matsubara (or, Baym-Kadanoff) GF in the \(\chi_{jL}\)-representation reproduced Eq.10 automatically. The latter means that we have to define the field operators in a proper way, then, using this definition, to calculate the commutation relations between them and rewrite the full secondary quantized Hamiltonian in this representation. Then we will use
these fermion operators for constructing the many-electron operators, which describe SEC, while the elementary commutation relations for these fermions will be used for calculation of the commutation relations between different complex combinations of them, which arise in the theory. In the second step we will separate the Hubbard-Anderson model from the full Hamiltonian. This should help to clarify the microscopical origin of the parameters of these models, and the nature of remaining Coulomb interactions. In third step we will generalize the Baym-Kadanoff formalism to the case of these complex non-Fermi and non-Bose operators which are generated by the equations of motion.

In cellular methods of AIBST the Bloch functions $\varphi_{k\lambda}(r)$ of the band $\lambda$ are often represented in the form of expansion over site-centered functions $\chi_{jL}(r) \equiv \chi_L(r - R_j)$. Here $L$ is complex index: $L = \{l, m, \sigma\}$. The secular equation in this representation has the form:

$$
(EO_{jL,j_1L_1} - h_{jL,j_1L_1})\chi_{j_1L_1}(r) = 0;
$$

(7)

here $O_{jL,j_1L_1} \equiv \langle \chi_L | \chi_{j_1L_1} \rangle$ is overlap matrix. The functions $\varphi$ and $\chi$ are connected by relation

$$
\varphi_{k\lambda}(r) = \sum_{\alpha jL} \tilde{u}_{\alpha}^* \chi_L^\alpha(k)e^{ikR_j} \chi_L(r - R_j) \equiv \sum_{jL} u_{k\lambda}^{jL}\chi_{jL}.
$$

(8)

The coefficients $Z$ here come from the Choleski’s factorization of the overlap matrix, $O = \bar{Z}Z$, while the Hamiltonian $\tilde{h}$ of corresponding secular problem,

$$
\tilde{h}_{\alpha\alpha'}(k)\tilde{\phi}_{\alpha\alpha'}(r) = E_{\alpha}(k)\tilde{\phi}_{\alpha\alpha}(r)
$$

(9)

is connected with the matrix element $h$ as follows:

$$
\tilde{h}_{\alpha\alpha'}(k) = \sum_{LL'} [\bar{Z}^{-1}(k)]_{LL'}^\alpha^\alpha' h_{LL'}(k)[Z^{-1}(k)]_{LL'}^{\alpha'}.
$$

(10)

At last, the equation for corresponding to the Eq.7 fermion GF $F$ has the form:

$$
(EO - h)_{jL,j'LL'} F_{j'LL',jL'} = \delta_{jj'}\delta_{LL'}.
$$

(11)

Having known the expression for $\varphi$ it is easy to find definition for $a_{jL}$. Let us insert Eq.8 into expansion for the field operator (4):
\[
\psi_1(r) = \sum_{k\lambda} \left[ \sum_{\alpha \ jL} \tilde{u}_{\alpha}^{*}(k)Z_{L}^{\alpha}(k)e^{ikR_j}\chi_{L}(r - R_j) \right] a_{k\lambda} = \\
\sum_{jL} \chi_{jL} \left[ \sum_{k\lambda} \tilde{u}_{\alpha}^{*}(k)Z_{L}^{\alpha}(k)e^{ikR_j}a_{k\lambda} \right] \equiv \sum_{jL} \chi_{jL} a_{jL},
\]

i.e., the operator of destruction of electron on the orbital \((jL)\) should be defined as the following combination of normal band operators:

\[
a_{jL} = \sum_{k\lambda} u^{jL}_{k\lambda} a_{k\lambda}.
\]

It follows from this definition that the anticommutator of these operators is equal to the inverse of the overlap matrix:

\[
\{a_{jL}, a_{j' L}^{\dagger}\} = (O^{-1})_{jL,j' L'},
\]

\[
O_{jL,j' L'} = \langle \chi_{jL} | \chi_{j' L'} \rangle.
\]

Since in practical calculations only finite number of the functions \(\chi_{jL}\) can be used, it is clear that the accuracy of this approximation is determined by the possibility to represent \(\delta\)-function in terms of the functions \(\chi\), namely,

\[
\delta(x - x') \approx \sum_{jL,j' L'} \chi_{jL}(x)O_{jL,j' L'}^{-1} \chi_{j' L'}^{*}(x'),
\]

The terms containing \(\psi_2\) can always be taken into account additionally. From a technical point of view the case of \(f\)-electrons differs from the case of \(d\)-electrons only by the number of correlated orbitals involved, at least in the initial steps. Let us now discuss the case of \(f\)-electrons and use for the operator \(a_{jL}\) with \(L = \{l = 3, m_l, \sigma\}\) the notation \(f_{jm_l}\sigma\), whereas all the non-\(f\)'s are called \(c_{jL}\), \(a_{jL} = \delta_{L,(3,m_l)\sigma}f_{m_l}\sigma + (1 - \delta_{L,(3,m_l)\sigma})c_{jL}\). Then the LDA part of the Hamiltonian can be written in the form:

\[
H_{LMTO} = \sum_{k\lambda} \epsilon_{k\lambda} a_{k\lambda}^{\dagger} a_{k\lambda} = \sum_{jL,j' L'} H_{jL,j' L'} c_{jL}^{\dagger} c_{j' L'} + \sum_{j,m_l,\sigma} \epsilon_{j}^{0} f_{jm_l\sigma}^{\dagger} f_{jm_l\sigma} + \\
\sum_{jm_l\sigma,j' m_l'\sigma} f_{jm_l\sigma}^{\dagger} f_{jm_l\sigma} f_{j' m_l'\sigma}^{\dagger} f_{j' m_l'\sigma} + \\
\sum_{jL,j' m_l,\sigma} [H_{jL,j' m_l,\sigma}^{\dagger} f_{j' m_l\sigma} + H_{jL,j' m_l,\sigma} f_{jm_l\sigma}^{\dagger}].
\]
Here the hopping matrix element and the position of the center of the $f$-band are given by:

$$t_{j,m,j',m'}^{\sigma} = \sum_k e^{i(k-R_j-R_j')} [H_{m_\sigma,m'_\sigma}(k) - \delta_{m_\sigma,m'_\sigma} \epsilon_0^f]$$

$$\epsilon_0^f = \sum_k H_{m_\sigma,m_\sigma}(k).$$

(16)

In the case when in ab initio band structure calculations (AIBST) the $f$-electrons have been treated as core electrons, $\epsilon_0^f$ is just single-electron level in the ”LDA”-atom, since in this case hopping and mixing are set equal to zero. Clearly, we are not allowed to diagonalize this Hamiltonian directly, since we deal with a non-orthogonal basis set.

Let us now write down the equation of motion for the Matsubara’s Green’s function (GF)

$$G_{jL,j'L'}(i\omega_n) = -i \langle T[a_{jL}(t)a_{j'L'}^{\dagger}(t')] \rangle_{\omega_n},$$

(17)

in this representation. We find that in the zero order approximation this equation has the desired form

$$[i\omega_n O_{jL,j'L'} - H_{jL,j'L'}] G_{jL,j'L'}(i\omega_n) = \delta_{j,j'} \delta_{L,L'},$$

(18)

since the expression in the square brackets exactly reproduces the matrix of the LDA secular problem.

In order to avoid confusion we remind that, as follows from Eqs. (11?) and (14?), a straightforward diagonalization of the matrix $H_{jL,j'L'}$ would lead to eigenvalues which do not coincide with the band-structure ones since the functions $\chi_{jL}$ are not orthogonal to each other, $\langle jL|j'L' \rangle = O_{jL,j'L'} \neq \delta_{j,j'} \delta_{L,L'} (!)$, and the overlap matrix $O$ is hidden in the commutation relations (14).

The other warning is the following: although the poles of the GF in Eq.11 coincide with the eigenvalues of the Kohn-Sham secular problem (what we want to have here), one cannot obtain the total energy $E_{tot}$ from the standard formula via GF and its self-energy. Therefore, the LDA potential in the equation for GF cannot be considered as self-energy.

The density of charge $\rho_{\sigma}(x)$ which enters the $H_{LDA}$, can be found, as usual, from GF (10),
\[
\rho_\sigma(x) = \langle \psi_\sigma^\dagger(x) \psi_\sigma(x) \rangle \approx \langle \psi_{1,\sigma}^\dagger(x) \psi_{1,\sigma}(x) \rangle = \lim_{t' \to t} \sum_{jL,j'L'} \chi_{jL}^\dagger(x)\chi_{j'L'}(x)G_{jL,j'L'}(t,t').
\]

As seen from (5-6) the perturbation theory from weak-coupling limit can be constructed with respect to deviations \((H - H_{LDA})\). In the case of expansion near atomic limit this is not possible.

**B. Many-electron representation and periodical Anderson model.**

A guiding idea on how to introduce this representation can be obtained from the known considerations of the s-band Hubbard model. Namely, the decomposition of the fermion operator \(c_\uparrow = c_\uparrow \cdot (1 - \hat{n}_\downarrow) + c_\uparrow \cdot \hat{n}_\downarrow\), is produced by the Hubbard repulsion which makes energies of the transitions \(c_\uparrow(1 - \hat{n}_\downarrow)\) and \(c_\uparrow \hat{n}_\downarrow\) different. The physical meaning of this decomposition is that every electron should "know" about populations of other orbitals at the same site. It is clear from this speculation that, as an example, for an \(f\)-electron in the orbital \(m_f = -3, \sigma = \uparrow\) we have to take into account in the corresponding decomposition as sum of all possible products:

\[
f_{-3,\uparrow} = f_{-3,\uparrow} \cdot (1 - \hat{n}_{-2,\uparrow}) \cdot (1 - \hat{n}_{-1,\uparrow}) \cdot ... \cdot (1 - \hat{n}_{+3,\downarrow})
+ f_{-3,\uparrow} \cdot \hat{n}_{-2,\uparrow} \cdot (1 - \hat{n}_{-1,\uparrow}) \cdot ... \cdot (1 - \hat{n}_{+3,\downarrow})
+ \cdots
+ f_{-3,\uparrow} \cdot \hat{n}_{-2,\uparrow} \cdot \hat{n}_{-1,\uparrow} \cdot ... \cdot \hat{n}_{+3,\downarrow} \tag{19}
\]

This transformation is, obviously, identical. In the next step, inserting this into the total Hamiltonian we take into account correlations by making use of the properties of the Fermi operators: \(f^2 = (f^\dagger)^2 = 0, \hat{n}^2 = \hat{n}\). The sums of the diagonal terms in the Hamiltonian, which have the same operator structure, give energies of corresponding many-electron states in the zero approximation. This step is still exact. However after this transformation returning to the form (6) and (15) of the Hamiltonian becomes somewhat difficult. The fermion GF in the atomic limit now acquires the form\[12\].
\[ F_{\nu}^{(at)}(i\omega) \equiv \langle T f_{\nu} f_{\nu}^\dagger \rangle |_{i\omega} = \sum_{\{\Gamma_n\}} \frac{\langle |\Gamma_n f_{\nu} | \Gamma_{n+1} \rangle^2 (N_{\Gamma_n} + N_{\Gamma_{n+1}})}{i\omega - (E_{\Gamma_{n+1}} - E_{\Gamma_n})}, \]  

(20)

where the spectral weights, say, for \( d \)-electrons, contain non-decoupled correlators, like

\[ N_{\Gamma_{n+1},\nu} \equiv \langle (1 - \hat{n}_1)(1 - \hat{n}_2) ... (1 - \hat{n}_{\nu-1}) \hat{n}_\nu (1 - \hat{n}_{\nu+1}) ... (1 - \hat{n}_{10}) \rangle \]

(21)

and so on. Here \( E_{\Gamma_n} \) is energy of \( n \)-electron configuration \( \Gamma_n \) of \( d(f) \)-ion. The transitions, described by different terms in this expansion, have different energies, and the energy separation between different terms is often so large, that their contribution to almost all observables is negligible. These terms can be neglected without changing the physics. The new reduced Hamiltonian can still be treated within a single-electron approximation, if we put all population numbers of the \( f \)-orbitals equal to integer numbers (0 or 1). The procedure, described above, actually, gives a formal derivation for the approach, exploited usually in band structure calculations for materials with well-localized \( 4f \)-electrons: \( f \)-electrons are placed in the core and their occupation number is taken to be equal to an integer number. For \( d \)-s and \( 5f \)-s, and even for the first part of \( 4f \)-series this procedure is often not sufficiently accurate. Thus, if either mixing or hopping are allowed, or some of the many-electron states have close energies, we come to the case of strong electron correlations. The key question is, of course, how large is Hubbard \( U \) in a particular compound with \( d \)- or \( f \)-electrons under interest. It should be noted that the definition of this magnitude and the way of calculation of it in different papers is different. Hubbard in his first paper, i.e. just the matrix element, which stands in the Hamiltonian. Note, however, that if it is convenient, any "preliminary" value can be chosen for \( H_0 \), since it will be taken into account later via \( H - H_0 \). Sometimes the shift \( U \rightarrow U_{\text{model}} \) is desirable, since this decreases the strength of perturbation. Since we started from an exact Hamiltonian, we have an opportunity to calculate \( U_{\text{model}} \) in terms of Coulomb interactions, existing in the system. We will return to this question after including Coulomb interaction into our diagram technique.

As we noted above, an alternative way to transform the Hamiltonian to the many-electron form, which describes the correlated motion of \( f \)-electrons in the case of Russel-Saunders type of coupling used by Irkhin. After the transformation is done, the terms
in the expansion, which clearly give small contribution can be neglected (for example, one can hardly expect that the Ni ion can be found in 5− or 6−valent states). Below we will use an equivalent, but more convenient way, compared to the above described method, to introduce the many-electron representation.

In the following part of this section we shall perform the following three steps: 1. Introduce a many-orbital representation. 2. Rewrite our Hamiltonian in this representation. 3. Separate out the main terms of the perturbation Hamiltonian. These steps will allow us to derive microscopically the multi-orbital periodic Hubbard-Anderson model for this particular representation.

Let us now construct the orbital representation for atomic states. It is convenient to use the following short notations for the $f$-orbitals. The orbitals with spin ”up” starting from $m_l = -3$ to $m_l = 3$ we shall label by $\mu = 1, 2, ..., 7$, whereas the ones with spin ”down” from $m_l = -3$ to $m_l = 3$ by $\mu = 8, ..., 14$. For instance, $|m_l = -2, \downarrow\rangle \equiv |\mu = 9\rangle$. The states of an $f$-ion with different number of electrons in the $f$-shell will be described in the orbital representation as $|\Gamma_0\rangle \equiv |0\rangle$, $|\Gamma_\mu\rangle \equiv |\mu\rangle = f^\dagger_\mu |0\rangle$, $|\Gamma_{\mu,\nu}\rangle \equiv |\mu, \nu\rangle = (\theta_{\nu\mu} f^\dagger_\mu f^\dagger_\nu |0\rangle + \theta_{\nu\mu} f^\dagger_\nu f^\dagger_\mu |0\rangle)$ and so on. Here $\theta_{\nu\mu} = 1$ if $\nu < \mu$ and $\theta_{\nu\mu} = 0$ if $\mu < \nu$. In other words, the following convention about the order of orbitals in any many-particle state $|\Gamma_n\rangle \equiv |\mu_1, \mu_2, ..., \mu_n\rangle \equiv f^\dagger_{\mu_1} f^\dagger_{\mu_2} ... f^\dagger_{\mu_n} |0\rangle$ is taken: $\mu_1 < \mu_2 < ... < \mu_n$ always holds. The advantage of the orbital representation is that it presents the simplest possible way to transform the Hamiltonian to the atomic representation and gives a very simple form for zero fermionic Green’s functions. Another advantage is that almost all rare earths have single-determinant ground state. On the other hand, the set of wave functions $|\Gamma_n\rangle$ is a complete set for any fixed $n$, therefore, more complicated states can be easily combined of these wave functions. This representation can be good starting point for description of $d$-electrons in $3d$-materials or for $5f$-electrons in actinides. For the case of $4f$-electrons the Russel-Saunders coupling should be used, i.e. many-electron states have to be constructed according to the scheme (see recent review by Irkhin and Irkhin [21] and references therein):
\[ |\Gamma_n\rangle = A_{\Gamma_n}^\dagger |0\rangle = \frac{1}{\sqrt{n}} \sum_{\gamma, \Gamma_{n-1}} G_{\Gamma_{n-1}}^{\Gamma_n} C_{\Gamma_{n-1}}^{\Gamma_n} f_{\mu}^\dagger A_{\Gamma_{n-1}}^\dagger |0\rangle \]  

(22)

where \( G_{\Gamma_{n-1}}^{\Gamma_n} \) are fractional parentage coefficients (\( \alpha \) is Rakah’s seniority), and \( C_{\Gamma_{n-1}}^{\Gamma_n} \) are Clebsch-Gordan coefficients. For actinides LS-coupling should be used (with spin-orbit coupling and other relativistic terms added). For 3d-materials, probably, crystal-field combinations are a proper choice. Thus, since different materials require different combinations of wave functions (or, operators), below we will use general notation for expansion of \( f \)-operators, so that a combination needed for diagonalization of \( H_{ion} \),

\[
H_{ion} = \sum_{j\mu} \epsilon_{j\mu} a_{j\mu}^\dagger a_{j\mu} \\
+ \frac{1}{2} \sum_{\mu_1, \mu_2, \mu_3, \mu_4} U_{\mu_1, \mu_2, \mu_3, \mu_4} a_{j\mu_1}^\dagger a_{j\mu_2}^\dagger a_{j\mu_3} a_{j\mu_4} - \sum_{\mu_1, \mu_2} v^{(LDA)}_{\mu_1, \mu_2} a_{j\mu_1}^\dagger a_{j\mu_2},
\]

(23)

is assumed to be used. Here the \( \epsilon_{\mu} \) are core and \( f \)-levels from LDA-calculation. Note, that in the case of Russel-Saunders coupling the Coulomb part of interaction can be rewritten in terms of Slater integrals and conveniently separated into the terms describing spin-spin, orbital-orbital interactions, etc.  

Let us now introduce a description in terms of the Hubbard’s operators \( X^\Gamma_{\Gamma'} = |\Gamma\rangle\langle\Gamma'| \). In order to see explicitly the process involved in the particular term of perturbation theory, it is convenient to use different notations for the diagonal and non-diagonal operators, distinguishing also quasi-fermionic and quasi-bosonic operators: For diagonal operators we use the notation: \( \hat{h}_{\Gamma} \equiv |\Gamma\rangle\langle\Gamma| \). For non-diagonal Fermi-like we use the notation: \( X_{\Gamma n, \Gamma' n+1} \equiv |\Gamma_n\rangle\langle\Gamma'_{n+1}| \). For non-diagonal Bose-like, with no change in the number of particles, we use \( Z: Z_{\Gamma n, \Gamma' n} \equiv |\Gamma_n\rangle\langle\Gamma'_n| \) and for Bose-like operators where the number of particles changes by an even number we use \( Z_{\Gamma n, \Gamma' n+2} \equiv |\Gamma_n\rangle\langle\Gamma'_{n+2}| \). Below we shall use also shorter notations for the transitions; for the Fermi-like transitions we denote \( X^a \) with \( a \equiv [\Gamma_n, \Gamma'_{n+1}] \), and for Bose-like transitions we use capital as superscripts: \( Z^\xi \) with \( \xi \equiv [\Gamma_n, \Gamma'_n] \) (including \( h^\Gamma \equiv Z^{\Gamma, \Gamma} \), or \( A \equiv [\Gamma_n, \Gamma'_{n+2}] \). The transitions in opposite direction will be denoted by a bar: \( \bar{a} = [\Gamma'_{n+1}, \Gamma_n] \). We also introduce special notations for the anticommutator of
X-operators and its average:

\[ \{ X_j^a, X_j^b \} = \hat{Q}_j^{ab} \quad \text{and} \quad \langle \{ X_j^a, X_j^b \} \rangle = Q_j^{ab} \quad \text{with} \quad \langle \hat{A} \rangle = \frac{Tr Ae^{-\beta H}}{Tr e^{-\beta H}}, \]  (24)

Here \( \beta = 1/T \), and \( T \) is the temperature in units \( k_B = 1 \). The fermion operator can be written in this representation as

\[ \hat{f}_{i\gamma} = (f_{\gamma})^a X_i^a = \sum_{\gamma_1} f_{0,\gamma_1}^a X_i^{0,\gamma_1} + \sum \Gamma X_i^\gamma + \sum \Lambda X_i^{\gamma,\Lambda} + \ldots, \]  (25)

where \( \gamma \) describes single-electron states, \( \Gamma \) and \( \Lambda \) stand for two- and three-particle states correspondingly. The matrix elements \( f_{0,\gamma_1}^a = (0|\hat{f}_{\gamma_1}|\gamma_1) \), \( f_{\gamma}^\gamma = (\gamma'|\hat{f}_{\gamma_1}|\Gamma) \), \( f_{\Gamma}^\Lambda = (\Gamma'|\hat{f}_{\gamma}|\Lambda) \) of the fermion operator \( \hat{f}_{\gamma} \) (using many-electron states \( |A\rangle = |\gamma\rangle,|\Gamma\rangle,|\Lambda\rangle \)) describe selection rules and reflect the representation chosen for description of \( f(d) \)-states: \( j - j^- \), Russell-Saunders coupling or the orbital one. In the case when the \( f \)-(non-\( f \)) overlap integrals are neglected, these coefficients acquire the simplest form in the orbital representation. For example, \( \langle \gamma'|\hat{f}_{\gamma}|\Gamma \rangle \neq 0 \) only if \( |\Gamma\rangle = |\gamma\gamma\rangle \). Therefore, in the expansion (25) the sum over double-electron states \( \Gamma \) is actually, \( \sum \gamma X^{\gamma,(\gamma',\gamma)}(1-\delta_{\gamma',\gamma}) \). In the last term in (Eq.25) the summation over three-particle states \( \Lambda \) includes only the states with \( \Lambda = (\Gamma',\gamma) \). Thus, the sum over \( \Gamma' \) contains only those of states \( \Gamma' \), which do not enter the second term of Eq.(25). For the rare earth ions the \( f \)-electron coefficients of expansion over \( X \)-operators can be expressed via Clebsch-Gordan and fractional parentage coefficients \[ x^n_{\Gamma}^{\Gamma_1} = \sqrt{nG_{\Gamma}^{\Gamma_1}} C_{\Gamma_1}^{\Gamma} \] However, when either \( f \)-orbitals of different sites, or \( f \)- and (non-\( f \))-orbitals, are not orthogonal to each other, these coefficients contain inversed overlap matrices. The Hubbard’s representation, taking into account correlations, builds into the theory the physical fact that in a system with SEC around atomic limit, the single electron transition, described by a fermion operator, does not exist as a simple one-electron excitation. Instead it is split into many intra-ion transitions. Formally this expansion includes the transitions between all states with \( (n+1) \)and \( n \) electrons. However, as was pointed out by Hubbard, the terms with large deviation of the population number \( n_f \) from its equilibrium value are separated by a very large energy gap from the ground state and therefore, if they even exist at all,
they do not give contribution to the formation of a crystal (and even liquid).

Let us change every $f$-operator in the total Hamiltonian by its expression in terms of $X$-operators (Eq.25) and separate the intra atomic part. The terms of Hamiltonian which contain more than one Hubbard operator, belonging to the same ion, should be simplified according to the multiplication rule for Hubbard’s operators, $X_j^{pq}X_j^{rs} = \nu_{qr}X_j^{ps}$, what takes strong interactions into account algebraically (here $\nu_{qr} = \langle q | r \rangle$ is sum determinants consisting of matrix elements of corresponding to these states inversed overlap matrices; $\nu_{qr} \neq \delta_{qr}$ if $\hat{O}^{-1} \neq \hat{I}$.

After that we have to collect the terms which have the same operator structure. Performing this transformation with the LDA-part of the Hamiltonian (6), and adding the $f-f$-Coulomb single-site interaction, we come to the first-step” Hubbard-Anderson model:

$$H_0 = \sum_{i,G} \tilde{E}^G_i \Gamma_i + \sum_{jL,j'L'} H_{jL,j'L'} c_j^{\dagger} c_{j'}^{\dagger},$$

$$H_{int}^{PHAM} = \sum \ell_{j'j}^{ab} X^a_j X^b_j + \sum W_{jL,j'L'a} c_{jL}^{\dagger} X^a_j + H.C.$$ (26)

The matrix elements of the Hamiltonian are discussed in Appendix A.

We need also the expression for the total number of electrons in this representation:

$$\hat{N}_e = O_{j_1L_1,j_2L_2} c_{j_1L_1}^{\dagger} c_{j_2L_2} + O_{j_1L_1,j_2M_2}(f_{M_2})^a c_{j_1L_1}^{\dagger} X^a_{j_2}$$

$$+ O_{j_1M_1,j_2L_2}(f_{M_1})^a X^a_{j_1} c_{j_2L_2} + (\hat{n}_M)_{T} \Gamma_\Gamma h^\Gamma_j$$

$$+ (1 - \delta_{j_1j_2})(f_{M_1})^\dagger c_{j_1M_1}^{\dagger} X^a_{j_1} X^a_{j_2}. (28)$$

As seen in the equations above, due to the non-orthogonality between states, part of the electrons are in mixed states.

Now our Hamiltonian is fully defined, i.e. the operator structure is derived and a recipe for a calculation of all matrix elements has been given. This allows us to continue to the next step, i.e. to the construction of the diagram technique. The reason why we call the Hamiltonian (26-27) as the ”first-step” one is that remaining terms of Coulomb interaction renormalize these parameters. We will return to this question later. First we will consider
the Hubbard-Anderson Hamiltonian. As we said, due to very large number of terms in full Hamiltonian we will construct first the diagram technique for the Hubbard-Anderson Hamiltonian, Eqs. (26),(27). After that we will return to Coulomb interaction.

III. DIAGRAM TECHNIQUE

A. Commutation relations

Since our aim here is to calculate the spectra and spectral weights of the quasi-particles by means of Green’s functions, the commutation relations between the operators involved is a necessary ingredient. Let us start from the fermion-like excitations and derive the equations of motion \( i \partial_t A = [A, H] \) for the operators \( A = c_{jL}, X^a_j \) for the case when these operators for different sites neither anticommute with each other nor commute with \( h^\Gamma \).

The correlations here manifest themselves via commutation relations on the site, to which the \( f \)-electrons under discussion belong. The results of a commutation \( [X^a_j, h^\Gamma_j] \), (which gives two Fermi-like \( X \)-operators), and an anticommutation \( \{X, X^\dagger\} \), (which gives Bose-like operators \( h, Z \)) are properties of the particular algebra used. It is convenient to have this information, written in terms of the structure constants of the correspondent algebra:

\[
\{X^a, X^b\} = \varepsilon^{a,b}_\Gamma h^\Gamma + \varepsilon^{a,b}_A Z^A + \varepsilon^{a,b}_A Z^A \equiv \sum_{\xi=\Gamma,A,A} \varepsilon^{a,b}_\xi Z^\xi, \quad (29)
\]

\[
[X^a, h^\Gamma] = \varepsilon^{a,\Gamma}_{a_1} X^{a_1}. \quad (30)
\]

When the interaction between \( X \)- and \( c \)-subsystems is switched off, in this particular (orbital) representation the constants \( \varepsilon \) can have values 0, 1, -1 and the upper indices show for which operators the (anti)commutator is calculated, while the lower index provides the right choice of all Hubbard operators for the r.h.s. of the (anti)commutator. In the case when \( X \)- and \( c \)-subsystems do interact and corresponding orbitals overlap, the constants \( \varepsilon \) in (29,30) contain sum of products of matrix elements of the inverse of overlap matrix (determinants) and are
given by quite cumbersome expressions. Usually, in physical situation, only some of $c$-electron bands have non-zero overlap with $f$-electron orbitals because of their location in different energy regions. For this reason one needs actually to take into account the overlap integrals only with those of $f$-orbitals which are located in the vicinity of Fermi energy, i.e. with upper subset of orbitally polarized $f$-shell. In order to give feeling of the structure of constants $\varepsilon$ we give a simple example in the Appendix B. These constants can easily be calculated for any given set of many-electron states. Below we will assume that $\varepsilon_{ab}^{\xi}$, etc., are calculated and known. One way to find the commutation relations is a straightforward calculation by making use of the facts that we know that

$$\{c_{jL,j'\mu,m_\sigma},(O^{-1})_{jL,j'\mu,m_\sigma}\}, \quad (31)$$

and any of the operators $X^a$ or $h^\Gamma$ can be expressed in terms of $f, f^\dagger$-operators. For example, using the general expansion

$$\hat{Y}_j = \sum_{\Gamma \Gamma'}\langle \Gamma|\hat{Y}_j|\Gamma'\rangle X^{\Gamma \Gamma'}, \quad (32)$$

and explicit expression for the operator of annihilation of electron on the third orbital in the state with second and third orbitals occupied, we see that

$$(1 - \hat{n}_1)\hat{n}_2\hat{f}_3(1 - \hat{n}_4)...(1 - \hat{n}_{14}) = -X^{(2)(23)}. \quad (33)$$

This direct way of calculation is quite long. There is, however, a way to make it compact. It is easy to verify that one can work with the operator $\sum_{jL} O_{j'\mu,jL}c_{jL}$ under an anticommutator sign (as one can with $f_{j'\mu}$ (here $\mu \equiv (m_\xi, \sigma)$ ). This observation immediately leads to the formula

$$\{c_{jL}, X^a_j\} = \sum_{a_1 m'_\alpha, \xi = A, \bar{A}, \Gamma} \sum_{a_2 m''_\alpha'} (O^{-1})_{jL,j'\mu,m_\sigma}(f_{m'_\alpha'})^{a_1,\xi} Z^{\xi}_{j'}^{a_2,\bar{A}}, \quad (34)$$

which reproduces the one we calculate in a straightforward way from the the expression for the $X$-operator in terms of $f, f^\dagger$-operators. The sign of each term in the sum over $a_1$ is determined by the matrix element $(f_{m'_\alpha'})^{a_1,\xi}$, which takes into account the convention about
the order of $f$-operators in a $|\Gamma\rangle$-state automatically. The same argument leads to the following expression for the commutator with $h^\Gamma$:

$$\left[c_{jL}, h^\Gamma_j \right] = \sum_{\alpha_1 m'_i \sigma'} (O^{-1})_{jL,j'm'_i\sigma'} (f_{m'_i\sigma'})^{\alpha_1} \varepsilon^{\alpha_1}_{b} \Gamma X^b_j.$$  \hspace{1cm} (35)

In the non-interacting system ($H_{\text{int}} = 0$) inverse processes of excitations are absent since $\{c, f\} = 0$. This anticommutator, of course, cannot be changed by $H_{\text{int}}$. However, the partial anticommutators $\{c, X^a\}$ may be non-zero, if they are considered separately. As it will be seen later, these anticommutators may involve two-particle processes.

Since the majority of rare-earth-based materials have a single-determinant ground state, it is quite obvious that the orbital representation is convenient for the description of ground-state properties. The excited states, however, are described in most cases by many-determinant states (in quantum-chemistry language described as "configurational interaction") and, therefore, the procedure of constructing the states $|\Gamma_n\rangle$, discussed in details by Irkhin and Irkhin should be used. In these cases the structure constants $\varepsilon^{ab}_c$ and so on, which come from the commutation relations, and the matrix elements $(f_{m_i\sigma})^{\alpha} = (f_{m_i\sigma})^{\Gamma_n,\Gamma_{n+1}} = \langle \Gamma_n | f_{m_i\sigma} | \Gamma_{n+1} \rangle$, include also the Clebsch-Gordon and fractional parentage coefficients. Here we will not go here into details of this well-developed theory and refer the reader to ref.18.

**B. S-matrix and the exact equations for GFs in functional derivatives.**

1. **Quasi-fermions**

   Now we introduce the Matsubara’s Green’s function (GF) for the fermion-like transitions. The idea, exploited in Refs. for the derivation of the diagram technique, is based on the possibility to express the terms, which come from interaction in the equation of motion for a GF, in terms of functional derivative of GF over external field, and, in the next step, on an iteration procedure. The equations of motion for Fermi-like and Bose-like operators are given in Appendix C. As seen from these equations (Eqs (C5-C16)), in our case the Hamiltonian...
generates the terms with the operator $\hat{Q}_{j}^{ac}$. Therefore, we have to introduce a type of external field $U(t)$ which generates this operator. However, an inspection of the further steps in such a version of the theory shows that using the field in the form $\int U_{j}^{ac}(t)\hat{Q}_{j}^{ac}(t)dt$ introduces information in a too much integrated form, which does not provide a possibility to calculate the quasi-boson GFs. Instead we introduce the definition for the quasi-fermion GF with different fields for different quasi-boson transitions;

$$\langle T\eta_{j\lambda}(t)\bar{\eta}_{j',\lambda'}(t') \rangle_{u} = \frac{\langle TS(-i\beta, 0)\eta_{j\lambda}(t)\bar{\eta}_{j',\lambda'}(t') \rangle}{\langle TS(-i\beta, 0) \rangle}. \quad (36)$$

The $S$-matrix is then defined as follows:

$$S(-i\beta, 0) = \exp\left\{ -i \int_{0}^{-i\beta} dt \left[ \sum_{j} U_{j}(t)Z_{j}(t) + \sum_{c} c_{jL}^{\dagger}(t)F_{jL,j',L'}(t)c_{j',L'}(t) \right] \right\}. \quad (37)$$

The additional terms which are generated by the external field $U$ and which should be added into the equations for the GFs are seen from the equation:

$$i\partial_{t}\{TS(-i\beta, t)\eta_{j\lambda}(t)S(t, 0)\} = \{TS(-i\beta, t)[i\partial_{t}\eta_{j\lambda}(t) + A_{j\lambda,j',\lambda'}(t)\eta_{j',\lambda'}(t)]S(t, 0)\}. \quad (38)$$

The elements of the matrix $A_{j\lambda,j',\lambda'}(t)$ are given in the Appendix D.

Second term, $c^{\dagger}Fc$, has the same operator structure as zero Hamiltonian of conduction electrons, $c^{\dagger}hc$; therefore, we will take them into account if in the equations of motion for any operator make exchange $\tilde{h}_{12} \rightarrow h_{12} = \tilde{h}_{12} + F_{12}$. Actually, we will need this field only for consideration of remaining terms of Coulomb interaction. On the other hand, it gives an additional convenient freedom to operate with equations for GFs.

As seen from the equations of motion (see Eqs.C5-C6) for the components of the $\eta$-operator, $c$- and $X$-operators, the equations for the GFs $\langle T\eta\bar{\eta} \rangle_{u}$ contain the Greens function $\langle TQ(t)\eta(t)\bar{\eta}(t') \rangle_{u}$ and $\langle T\eta(t)Q(t)\bar{\eta}(t') \rangle_{u}$ (see Eq.(C10-13)). Both these GFs can be obtained from the three-time GF $\langle TQ(t''')\eta(t)\bar{\eta}(t') \rangle_{u}$ by taking the corresponding limit, $\lim_{t''\rightarrow t+0}...$ or $\lim_{t''\rightarrow t-0}...$. Since $\hat{Q}_{\xi}^{ab} = \varepsilon_{\xi}^{ab}Z_{\xi}$, $\delta S/\delta U_{j\xi}(t) = -iSZ_{\xi}$, and

$$\langle TZ_{\xi}(t''')\eta(t)\bar{\eta}(t') \rangle_{u} \equiv \langle TZ_{\xi}(t''') \rangle_{u} + i\delta \frac{\delta}{\delta U_{j\xi}(t''')} \langle T\eta(t)\bar{\eta}(t') \rangle_{u}, \quad (39)$$
any of the three-time GFs can be expressed via functional derivative of the GF \( \langle T_\eta(t)\eta(t') \rangle_u \) over corresponding field \( U_j(t') \), another trick exploited by Schwinger\cite{Schwinger} and by Baym and Kadanoff\cite{BaymKadanoff}. After that the equations for the GFs can be written in closed form straightforwardly from the equations of motion for \( c- \) and \( X- \)operators, given by Eqs.C5 and C6, and the relation in Eqn.38. The diagonal expectation values of the diagonal operators, \( \langle h^\Gamma \rangle \) in the equilibrium state have physical meaning of population numbers of the ion’s state \( \Gamma \). When external time-dependent fields are present, these operators do not commute with the Hamiltonian even when the interaction is switched off, therefore, \( \langle h^\Gamma \rangle \), strictly speaking, cannot be interpreted as population numbers any more. Although it is not completely correct, for brevity we will refer loosely to “population numbers” for the expectation values of any Bose-like single-site operator.

For brevity we will not write the complete matrix equation for \( \langle \eta(t)\eta \rangle_u \), instead we will specify only the left-hand-side \( \eta- \)operator. Then we find that the equation for the set of GFs \( \langle Tc_j(t)\eta \rangle_u \) has the following form,

\[
\begin{align*}
\left[ \delta_{j,j_1} & \delta_{L,L_1} i \partial_t - (O^{-1}H)_{jL,j_1L_1} \right] \langle Tc_{j,L_1}(t)\eta \rangle_u - [A^{(cX)}_{jL,j_1b}(t) + w_{jL,j_1b}] \langle TX^b_{j_1}(t)\eta \rangle_u \\
&= A^{(cX^\dagger)}_{jL,j_1b}(t) \langle TX^b_{j_1}(t)\eta \rangle_u - i \langle \{c_{jL}, \eta \} \rangle_u \delta(t - t') \\
&+ O_{jL,j_1M}^{(cX)} \langle \{\hat{Q}^a_{j_1}(t^+) \rangle_u + i \frac{\delta}{\delta U^a_{j_1}(t^+)} W^{*}_{j_1a,j_2L_2} \langle Tc_{j_2L_2}(t)\eta \rangle_u \\
&+ O_{jL,j_1M}^{(cX)} \langle \{\hat{Q}^a_{j_1}(t^+) \rangle_u + i \frac{\delta}{\delta U^a_{j_1}(t^+)} t^{ab}_{j_1j_2} \langle TX^b_{j_2}(t)\eta \rangle_u \\
&- O_{jL,j_2M}^{(cX)} \langle \{\hat{Q}^a_{j_2}(t^-) \rangle_u + i \frac{\delta}{\delta U^a_{j_2}(t^-)} \rangle_u \\
&\times \{t^{ba}_{j_1j_2} \langle TX^b_{j_1}(t)\eta \rangle_u + W_{j_1L_1,j_2a} \langle Tc_{j_2L_2}(t)\eta \rangle_u \}.
\end{align*}
\]

The equation for the set of GFs \( \langle TX^b_{j}(t)\eta \rangle_u \) is

\[
\begin{align*}
[\delta_{ab}(i \partial_t - \Delta_{ja}) - A^{a}_{ja}(t)] \langle TX^b_{j}(t)\eta \rangle_u - A^{a}_{ja}(t) \langle TX^b_{j}(t)\eta \rangle_u \\
= i \langle \{X^a_{j}, \eta \} \rangle_u \delta(t - t') \\
+ \langle \hat{Q}^a_{j}(t^+) \rangle_u + i \frac{\delta}{\delta U^{ab}_{j}(t^+)} t^{bc}_{j_1j_2} \langle TX^c_{j_2}(t)\eta \rangle_u \\
+ \langle \hat{Q}^a_{j}(t^+) \rangle_u + i \frac{\delta}{\delta U^{ab}_{j}(t^+)} w^{*}_{j_1j_2L_2} \langle Tc_{j_2L_2}(t)\eta \rangle_u
\end{align*}
\]
\[-[\langle \dot{Q}_j^{ca}(t^-) \rangle_u + i \frac{\delta}{\delta U^{ca}_j(t^-)}] \]
\times \{t_{j1}^{\bar{b}c} \langle TX_j^{\bar{b}}(t) \bar{\eta} \rangle_u + w_{j1L_1,jc}^\dagger \langle Tc_{j1L_1}^\dagger(t) \bar{\eta} \rangle_u \}. \quad (41)

The equations for \( \langle Tc_{j1L_1}^\dagger(t) \bar{\eta} \rangle_u \) and \( \langle TX_j^{\bar{b}}(t) \bar{\eta} \rangle_u \) can be obtained from Hermitian conjugation of the corresponding equations of motion,

\[\begin{align*}
&\left[\left(-i\partial_t - \Delta_{ja} \right) - A^\alpha_{ja}\right] \langle TX_j^{\bar{b}}(t) \bar{\eta} \rangle_u - \langle TX_j^{b}(t) \bar{\eta} \rangle_u
\times \{t_{j2L_2,jL_1}^{\bar{b}a} \langle Tc_{j2L_2}^\dagger(t) \bar{\eta} \rangle_u + t_{j2jL_1}^{\bar{a}b} \langle TX_j^{b}(t) \bar{\eta} \rangle_u \} \right] \\
&= -i \langle \{X_j^{\bar{a}}(t^-) \} - A^\alpha_{ja}\rangle \bar{\eta} \rangle_u - \langle TX_j^{b}(t) \bar{\eta} \rangle_u
\times \{t_{j2L_2,jL_1}^{\bar{b}a} \langle Tc_{j2L_2}^\dagger(t) \bar{\eta} \rangle_u + t_{j2jL_1}^{\bar{a}b} \langle TX_j^{b}(t) \bar{\eta} \rangle_u \} \right] \\
&\times \left[\left(-i\partial_t - \Delta_{ja} \right) - A^\alpha_{ja}\right] \langle TX_j^{\bar{b}}(t) \bar{\eta} \rangle_u - \langle TX_j^{b}(t) \bar{\eta} \rangle_u
\times \{t_{j2L_2,jL_1}^{\bar{b}a} \langle Tc_{j2L_2}^\dagger(t) \bar{\eta} \rangle_u + t_{j2jL_1}^{\bar{a}b} \langle TX_j^{b}(t) \bar{\eta} \rangle_u \} \right] \\
&= -[\langle \dot{Q}_j^{ab}(t^-) \rangle_u + i \frac{\delta}{\delta U^{ab}_j(t^-)}] \\
\end{align*}\]
\times \{w_{j2L_2,jL_1}^{\bar{b}b} \langle Tc_{j2L_2}^\dagger(t) \bar{\eta} \rangle_u + t_{j2jL_1}^{\bar{a}b} \langle TX_j^{b}(t) \bar{\eta} \rangle_u \} \right]. \quad (42)

The products \((HO^{-1})\) and \((O^{-1}H)\) are the matrix products in the cc-subspace only, i.e.

\[(HO^{-1})_{jL,j' L'} \equiv H_{jL,j,L'}(O^{-1})_{jL,j',L'}. \quad (44)\]

The labels \( \pm \) near the time variable denote limits \( t^\pm = t \pm 0^+ \).

2. Quasi-bosons

Our recipe for calculation of the GFs is so far not complete; we have to describe how to calculate the population numbers and their derivatives. The latter, actually, describe the
boson-like excitations in the system. Now we turn to the consideration of this part.

The "gauge" field coming from the source-term of the $S$-matrix is

$$A_j^{ξξ}(t) \equiv ε_{ξξ}^{ξξ} U_j^{ξξ}(t),$$

where $ε_{ξξ}^{ξξ}$, similar to Eqn.29, gives the coefficients of expansion $[Z^{ξ}, Z^{ξξ}] = ε_{ξξ}^{ξξ} Z^{ξξ}.

Let us write down first the equation for $⟨Z_j^{ξ}(t)⟩_u$. For that we have to add to the average of (54) the contribution from the source term. Then we find

$$[δ^{ξξ}(i\partial_t - Δ_ξ) - A_j^{ξξ}(t)]⟨TZ_j^{ξ}(t)⟩_u =$$

$$\sum_{n_1,λ_1, n_2, λ_2} V^{ξξ}_{n_1, n_2, λ_1, λ_2} ⟨Tη_{n_1, λ_1}(t)η_{n_2, λ_2}(t)⟩_u.$$ (46)

This equation is valid also for the case of diagonal transition, $⟨Z_j^{ξ,Γ}(t)⟩_u = ⟨h_j^{Γ}(t)⟩_u$. In this case $Δ_ξ = Δ_{Γ,Γ} = E_Γ - E_Γ = 0$ and at zero fields, $U = 0$, we come to the case of thermodynamical equilibrium,

$$i\partial_t ⟨Th_j^{Γ}(t)⟩ = \sum_{n_1, λ_1, n_2, λ_2} V^{ξ,Γ}_{n_1, n_2, λ_1, λ_2} ⟨Tη_{n_1, λ_1}(t)η_{n_2, λ_2}(t)⟩_u.$$ (47)

where the population numbers $N_Γ ≡ ⟨Th_j^{Γ}(t)⟩$ do not depend on time. Then, the right-hand side gives zero identically, since summation in the right-hand side of (47) produces the difference of Hermitian adjoints. This equation is useful for checking the approximation made but does not give a recipe for finding $N_Γ$. Therefore, we have to go further and to use connection between the GFs

$$⟨TZ_j^{ξ}(t)Z_j^{ξ'}(t')⟩_u ≡ K_j^{ξξ'}(t, t')$$ (48)

and their end-factors

$$P^{ξξ'}(t) ≡ ⟨T[Z_j^{ξ}(t), Z_j^{ξ'}(t)]⟩_u = δ_{jj'} ε_{ξξ}^{ξξ'} ⟨TZ_j^{ξξ'}(t)⟩_u.$$ (49)

Let us derive equations for the Bose-like GFs. They can be obtained in two ways. One way is to use the equations of motion, Eq.(C18) and then to connect the higher-order GF with the lower-order one via functional derivative. Another way is to take the functional derivative
The equations of motion give:

\[ \frac{\delta}{\delta \epsilon_j (i \partial_t - \Delta_\epsilon)} - A_j^{\epsilon \xi_2}(t) K_{j \xi_2, j \epsilon'}(t, t') = i \delta(t - t') P_{j j'}^{\epsilon \epsilon'}(t) + \]

\[ V_{n_1 \lambda_1, n_2 \lambda_2}^\xi \langle T \eta_{n_1 \lambda_1}^\dagger(t) \eta_{n_2 \lambda_2}(t) Z_{j j'}^{\epsilon \epsilon'}(t') \rangle_u \]  

(50)

Let us consider now the following three-time GF \( \langle T \eta_{n_2 \lambda_2}(t_1) \eta_{n_1 \lambda_1}(t_2) Z_{j j'}^{\epsilon \epsilon'}(t') \rangle_u \). On the one hand, the two-time GF in the last term of Eq.50 can be expressed as the limit

\[ \lim_{t_2 \to t + 0} \langle T \eta_{n_2 \lambda_2}(t) \eta_{n_1 \lambda_1}(t_2) Z_{j j'}^{\epsilon \epsilon'}(t') \rangle_u = \langle T \eta_{n_1 \lambda_1}(t) \eta_{n_2 \lambda_2}(t) Z_{j j'}^{\epsilon \epsilon'}(t') \rangle_u \]  

(51)

of this function. On the other hand, we can again use Eq.39 and express it in terms of the GF \( G = \langle T \eta_{n_2 \lambda_2}(t) \eta_{n_1 \lambda_1}(t_2) \rangle_u \). This gives the following equation for the boson-like GF:

\[ (L^0(t, t_1)^{-1})_{j \xi_2, j \xi_1} K_{j \xi_1, j' \epsilon'}(t_1, t') = i \delta(t - t') P_{j j'}^{\epsilon \epsilon'}(t) + \]

\[ \lim_{t_2 \to t + 0} V_{n_1 \lambda_1, n_2 \lambda_2}^\xi \langle TZ_{j j'}^{\epsilon \epsilon'}(t') \rangle_u + i \frac{\delta}{\delta U_{j j'}^{\epsilon \epsilon'}(t')} \langle T \eta_{n_2 \lambda_2}(t) \eta_{n_1 \lambda_1}(t_2) \rangle_u, \]  

(52)

where \( (L^0)^{-1} \) is defined by the equation:

\[ \{ [\delta_j^{\epsilon \xi_2} (i \partial_t - \Delta_\epsilon) - A_j^{\epsilon \xi_2}(t)] \delta(t - t_2) \} L^0_{j \xi_2, j' \epsilon'}(t_2, t') = i \delta(t - t'). \]  

(53)

The procedure which remains to be discussed is how to calculate the expectation values \( \langle TZ_{a b}(t) \rangle_u \), i.e., population numbers. The natural way to do that is to use the multiplication rule for the Hubbard operators \( X_{j}^{p, q} \cdot X_{j}^{r, s} = |j, p\rangle\langle j, q| \cdot |j, r\rangle\langle j, s| = \delta_{q, r} X_{j}^{p, s} \). In the limit \( t' \to t + 0 \) the GFs \( K(t, t') \) or \( G(t, t') \) contain a product of two operators at the same moment of time and, therefore, we can use the rule of multiplication. In the case of retarded GFs an application of the spectral theorem gives an equivalent system of equations in those of approximations, in which the analytical extension of the vertex corrections does not involve different values of vertexes from different time intervals:

\[ N_j^\Gamma = [\lim_{t \to t^+} \langle X_j^\dagger(t) X_j^\Gamma(0) \rangle], \]  

(54)

or from Bose-like GFs,
\[
N_j^\Gamma = \lim_{t \to +0} \langle Z_\xi(t) Z_j^\xi(0) \rangle_{i=j},
\]
where \( \xi = [\Gamma, \Gamma_1] \).

When the iterative perturbation theory at \( U(t) \neq 0 \) is used none of expectation values of \( \langle Z(t) \rangle \) is equal to zero. In the limit of thermodynamics \( U(t) = 0 \) the non-diagonal numbers \( \langle Z^\xi \rangle = 0 \) while the diagonal ones \( N_\Gamma \) and their derivatives \( \frac{\partial^n N_\Gamma}{\partial U_{\Gamma_1} \partial U_{\Gamma_2} \cdots \partial U_{\Gamma_n}} |_{U=0} \) are not. The derivatives of non-diagonal occupation numbers are charge and magnetic susceptibilities (see Eqs 94-95 below). However, the correlators \( \langle h^\Gamma h^\Gamma \rangle \) also contribute to both of them.

3. Comments on the system of equations

Eqs. 40-43 and 52 are the basic equations of our theory which we will use for generating a series of perturbation theory. The iterative terms and lowest approximations will be discussed in the next section. Within this formulation of the diagram technique the difference between the cases of orthogonal and non-orthogonal bases sets consists only in the number of interactions involved and in the definitions of the matrix elements. Contrary to the standard case of normal fermionic system the set of equations Eqs.40-43 for quasi-fermion transitions is not yet a complete set even in terms of functional derivatives, as seen from Eqs.41,52 and will be seen also later. The functional derivatives from expectation values of quasi-boson operators introduce also energy-dependent contributions to the self-energy from quasi-boson excitations and in addition, broadening of spectral weights. The difference to the case of, for instance, standard Fermi-liquid theory is that in the Fermi-liquid the boson excitations arise only as collective modes whereas in our case they exist even in the level of zero Hamiltonian. At first sight the presence of the GFs \( \langle T c_{j_2k_2}^\dagger(t) \bar{\eta}_{\eta \cdot} \rangle_u \) for \( \eta = c^\dagger \) in the system of equations looks somewhat strange since we are considering the normal, not superconducting state. Actually, the zero GFs of this kind are indeed equal to zero in the normal state; this is simply a manifestation of the fact that our external Bose-like field \( U \) contains components which describe the transitions \([\Gamma_n, \Gamma_{n\pm2}]\), i.e. transfer of 2 electrons simultaneously. The corresponding GF describes process of transformation of two conduction
electrons to \( f \)-electrons on the same site (or \textit{vice versa}) and appears only as a perturbational contribution. Thus, at zero external field we have \( \langle c^\dagger c^\dagger \rangle = 0 \) whereas \( \delta \langle c^\dagger c^\dagger \rangle / \delta U \) may have non-zero values. This, obviously, leads to the existence of some non-zero correlations of the kind \( \langle c_1 c_2(\tau)c_3^\dagger c_4^\dagger(\tau') \rangle \), and as a consequence superconducting fluctuations above \( T_c \) due to phonons. Some other mechanism which are described by the same function may also be influenced by the two-particle intra-atomic correlations (for example, it can make the solution with the \( d \)-wave symmetry of the order parameter more favorable compared to the one with \( s \)-symmetry\(^{43,44} \)).

IV. APPROXIMATIONS

Eqs. 40-43 and 52 can be used for iterations straightforwardly. However, since the subsystems of conduction electrons and quasi-atomic transitions are coupled, it is more convenient in practical calculations to make iterations from a more symmetrical form of these equations. Let us first rewrite the equations in terms of the operators \( \eta_1, \eta_1^\dagger \) with the indexes \( 1 \equiv (j_1, \lambda_1) \). In order to do this let us return for a moment to the initial Hamiltonian of PAM. All its terms except the one \( \mathcal{H}_0^f = \sum E_j^0 h_j^\Gamma \) can be expressed in terms of operators \( \eta_1, \eta_1^\dagger \),

\[
\mathcal{H}_{\text{int}}' = \eta_2^\dagger V_{23}^\dagger \eta_3 \equiv H_{23}^\dagger c_2^\dagger c_3 + W_{23}^\dagger c_2^\dagger X_3 + W_{23}^* X_2^\dagger c_3 + t_{23} X_2^\dagger X_3. \tag{56}
\]

The term \( \mathcal{H}_0^f \) does not cause difficulties since, as seen from Eqns.C5,C6 and C18, in the equations of motion it generates a term which also can be written in terms of \( \eta \)-operators. We denote this term as \( \theta_{12}^\Gamma : \theta_{12}^\Gamma \eta_2 \equiv [\eta_1, \sum E_j^0 h_j^\Gamma] \). Therefore, the equations for GFs, \( G_{12}(t, t') \equiv \langle T\eta_1(t)\eta_2^\dagger(t') \rangle_u \), can be expressed fully in terms of \( \eta \)-operators and functional derivatives of GFs with respect to external fields,

\[
(i\delta_{12} \partial_t - A_{12}(t) - \Omega_{12}^0 - \theta_{12}^\Gamma) G_{21'}(t, t') = iP_{11'}(t, t') + V_{23}(T\{\eta_1(t), \eta_2^\dagger(t)\}) \eta_3(t)\eta_1^\dagger(t') - V_{23}(T\eta_2^\dagger(t_1)\{\eta_1(t), \eta_3(t)\}) \eta_1^\dagger(t'), \tag{57}
\]

\[
V_{23}(T\eta_3^\dagger(t_1)\{\eta_1(t), \eta_3(t)\}) \eta_1^\dagger(t'), \tag{58}
\]
where $A_{jL,j'L'} = 0$. Since we have moved the non-$f$ part of the LDA Hamiltonian from zero Hamiltonian to the matrix of interaction $V$, $\Omega^0$ becomes a purely diagonal matrix:

$$\Omega^0_{12} = \Omega^0_{12} \delta_{12} : \Omega^0_{j_{a,j'b}} = \delta_{jj'} \delta_{ab} \Delta \bar{\alpha}, \quad \Omega^0_{j_{L,j'L'}} = \delta_{jj'} \delta_{LL'} \varepsilon^0_{L}. \quad (59)$$

Here we have included a $\delta$-function into the definition of the time-dependent population number,

$$P_{11'}(t_1, t'_1) \equiv \delta(t_1 - t'_1) \langle \hat{Q}_{11'}(t_1) \rangle \equiv \delta(t_1 - t'_1) P_{11'}(t'_1). \quad (60)$$

It is seen from Eqns.40-41 that in order to have a compact form of equations, we have to form combinations of the operators $\langle Q \rangle + i \frac{\partial}{\partial t}$ with matrix elements, such that they reproduce full combinations $\{\eta_1, \eta^\dagger_2\}, \{\eta_1, \eta_2\}$ in the equations of motion. The GFs of higher order in terms of Eqns.40 and 41, which are expressed in terms of functional derivatives, can be written in compact notations as follows:

$$V_{23} \langle T \{\eta_1(t), \eta^\dagger_2(t)\} \eta_3(t) \eta_{1'}(t') \rangle =$$

$$V_{23} [\hat{P}_{12}(t^+) + \hat{R}_{12}^l(t^+)] \mathcal{G}_{31'}(t, t'), \quad (62)$$

$$V_{23} \langle T \eta^\dagger_2(t_1) \{\eta_1(t_1), \eta_3(t_1)\} \eta_{1'}(t'_1) \rangle =$$

$$V_{23} [\hat{P}_{12}(t^-) + \hat{R}_{12}^r(t^-)] \langle T \eta^\dagger_2(t) \eta^\dagger_{1'}(t') \rangle_u. \quad (63)$$

The operators $\hat{R}$ are here defined in such a way that $\hat{R}_{12}^l(t^+) = 0$ and $\hat{R}_{12}^r(t^-) = 0$ for c-electrons, i.e., when $1 = (j_1, L_1)$ and $2 = (j_2, L_2)$. The cases when one of these indexes, 1, 2, or both of them describe $f$-electron transitions, are described with the help of the matrices $\alpha$ and $\beta$. They have to provide correct commutation relations and, therefore, we define them by the equalities:

$$\{\eta_1, \eta^\dagger_2\} = \bar{\alpha}^{m_1}_{12,3_3} Z_{3_3}, \quad \{\eta_1, \eta_3\} = \bar{\beta}^{m_1}_{12,3_3} Z_{3_3}, \quad \{\eta^\dagger_1, \eta^\dagger_3\} = \bar{\beta}^{m_1}_{12,3_3} Z_{3_3} \quad (64)$$

where $\xi = A, \bar{A}, \Gamma$, $\zeta = [\Gamma_n, \Gamma_{n+2}]$ and $\bar{\zeta} = [\Gamma_n, \Gamma_{n-2}]$. The complex index $3_b \equiv (j_3, \xi_3)$ in the case of the $\bar{\alpha}$-matrix, then, $3_b \equiv (j_3, \xi_3)$ in the case of $\bar{\beta}^{m_1}_{12,3_3}$-matrix, and, at last,
$3_b \equiv (j_3, \bar{\zeta}_3)$ for the $\beta_{12,3_b}^{\eta\eta^\dagger}$-matrix. The subindex “$b$” points out that the index runs over Bose-like variables. If, for example, $\eta = c$, and $\eta^\dagger = X^\dagger$, we have

$$\tilde{\alpha}_{12,3_b}^{cX^\dagger} = {O_{12}^{-1}} \delta_{23}(f_M)^{a}_{c\xi} \xi^a_{b},$$

and so on. We will not repeat all these definitions since they are clearly seen from the expressions given in Eqs.40-43. Then the operators $\hat{R}_{12}^l(t^+)$ and $\hat{R}_{12}^r(t^-)$ are:

$$\hat{R}_{12}^l(t^+) \equiv \lim_{t_4 \to t^+} \alpha_{12,3_b}^{\eta\eta^\dagger} \frac{\delta}{\delta U_j^\xi_j(t_4)} \equiv \lim_{t_4 \to t^+} \alpha_{12,3_b}^{\eta\eta^\dagger} \frac{\delta}{\delta U_3^\xi_3(t_4)},$$

$$\hat{R}_{12}^r(t^-) \equiv \lim_{t_4 \to t^-} \beta_{12,3_b}^{\eta\eta^\dagger} \frac{\delta}{\delta U_j^\xi_j(t_4)} \equiv \lim_{t_4 \to t^-} \beta_{12,3_b}^{\eta\eta^\dagger} \frac{\delta}{\delta U_3^\xi_3(t_4)},$$

where the relations between the matrices $\alpha$ and $\tilde{\alpha}$, $\beta$ and $\tilde{\beta}$ are as follows:

$$\alpha_{12,3_b}^{\eta\eta^\dagger} = (1 - \delta_{1,j_1L_1} \delta_{2,j_2L_2}) \alpha_{12,3_b}^{\eta\eta^\dagger}, \quad \beta_{12,3_b}^{\eta\eta^\dagger} = (1 - \delta_{1,j_1L_1} \delta_{2,j_2L_2}) \beta_{12,3_b}^{\eta\eta^\dagger}.$$

Defining in this way $\alpha$- and $\beta$-matrices in the $\hat{R}$-operators we put in a formal language the requirement that $\hat{R}_{12} = 0$ when both ends, 1 and 2, are c-electron ones. Further, as we remember, in Eqs.40-43 (see also here Eqs.78 and 81) the term $\langle T\eta_2^\dagger(t)\eta_1^\dagger(t')\rangle_u$ is expressed in terms of functional derivatives of the GF $\langle T\eta_2^\dagger(t)\eta_1^\dagger(t')\rangle_u$. The matrix of this GF consists of the same elements as the matrix $\langle T\eta_2^\dagger(t)\eta_1^\dagger(t')\rangle_u$. Therefore, we can express the former GF via the latter one as

$$\langle T\eta_2^\dagger(t)\eta_1^\dagger(t')\rangle_u = \tau_{23} G_{31}(t,t'),$$

where the matrix $\tau_{23}$ makes necessary permutations of the matrix elements and, therefore, consists of zeroes and unities only. For example, if we deal with a system which has $n$ conduction bands and $m$ intra atomic Fermi-type transitions, the matrix $\tau_{23}$ has all matrix elements equal to zero except over- and sub-diagonals where all the matrix elements are equal to one,

$$\tau_{(j_21,j_3n+m+1)} = \tau_{(j_22,j_3n+m+2)} = \cdots = \tau_{(j_2n+m,j_32(n+m))} = 1,$$

$$\tau_{(j_2n+m+1,j_31)} = \tau_{(j_2n+m+2,j_32)} = \cdots = \tau_{(j_22(n+m),j_3n+m)} = 1.$$
Note that the left \( t_1 \rightarrow t_1^+ \) and the right \( t_1 \rightarrow t_1^- \) limits are included into definitions of the operators \( R(t^+) \) and \( R(t^-) \) correspondently.

Let us now introduce the auxiliary zero GF \( D^{(0)} \) by the following equation:

\[
\int dt_2 \left[ \frac{1}{t} (\delta_{12} \partial_1 - A_{12}(t_1) - \Omega_{12}^0) \delta(t_1 - t_2) \right] D^{(0)}_{21'}(t_2, t_1') = \delta_{11'} \delta(t_1 - t_1').
\] (70)

As seen from (59), the matrix \( \Omega_{12}^0 \) has purely local, on-site, characteristics. Therefore, it is natural to call the function \( D^{(0)}(t,t') \) "locator". However, mixing, hopping and overlap connect different sites, which leads to dependence of the dressed locators \( D(t,t') \) on the variables of different sites; for this reason they will be named "pseudolocators". The inverse matrix of \( D^{(0)} \), i.e. \( [D^{(0)}_{12}(t_1, t_2)]^{-1} \equiv D^{-1}_{0}(1,2) \), is given by the expression in the square brackets on the l.h.s of Eq.98. Putting \( \theta = V = 0 \) in Eq.(57-58) for the full GF we obtain the equation for zero GF \( G^{(0)}_{21'}(t,t') \):

\[
\int dt'' D^{-1}_{0,12}(t,t'') G^{(0)}_{21'}(t'', t') = P^{(0)}_{11'}(t,t').
\] (71)

We will use this equation below for iterations. In this notation the full equation for the GF acquires the following form:

\[
\int dt_3 D^{-1}_{0,13}(t,t_3) G_{31'}((t_3, t')) - \left\{ \frac{1}{t} \eta_{13}^F + [P_{12}(t^+) + \hat{R}^l_{12}(t^+)] V_{23} - \frac{1}{t} V_{24} [\hat{P}_{14}(t^-) + \hat{R}^r_{14}(t^-)] \tau_{23} \right\} G_{31'}(t,t') = P_{11'}(t,t').
\] (72)

The same equation can be presented also in a way close to the standard form of the Dyson equation:

\[
\{ D^{-1}_{0,12}(t,t_2) - S_{12}(t,t_2) \} G_{21'}(t_2, t') = P_{11'}(t,t').
\] (73)

Here and below we omit the sign of integration over intermediate time (here \( t_2 \)). Eq. 73 gives the definition of the self-operator matrix \( S \). However, as seen, this equation does not fully coincide with the standard definition of self-energy. The difference between Eq.73 and the standard Dyson equation consists of the presence of \( P_{11'}(t,t') \) in r.h.s., instead of \( \delta_{11'} \delta(t,t') \) and is caused by the non-fermion commutation relations \( \{ \eta_1, \eta_2^\dagger \} \neq \delta_{12} \). As will
be seen later, these terms give rise to whole generation of new graphs. Part of graphs have the same structure that in the theory of fermions. The $S$-self-operator contains both type of graphs, of Fermi-liquid type, and the terms, generated by the right-hand side of Eqs. 72-73. In order to distinguish between them we use the term "self-operator" in definition for the full GF(23), while the term "self-energy" will be used in a more traditional way, for the set of graphs which renormalize the denominators of the pseudolocators, and will be introduced later. In order to separate these two type of graphs we will search the solutions of (73) in the form (71), i.e. we introduce the full pseudolocator $D$ by the Dyson equation

$$\{D_{012}^{-1}(t,t_2) - S_{12}(t,t_2)\}D_{21'}(t_2,t') = \delta_{11'}\delta(t-t').$$ (74)

Then the full GF is given by

$$G_{11'}(t,t') = D_{12}(t,t'')P_{21'}(t'',t') = D_{12}(t,t')P_{21'}(t').$$ (75)

(Note, that the population number $\mathcal{P}$ in the equation above depends on the right time $t'$).

The lowest approximation as well as the equation for the self-operator, which is convenient for iterations, can be obtained from its explicit expression in terms of functional derivatives. The equation for the self-energy follows from a comparison of the two forms of equations for the GF, one, Eqn.73, in terms of self-energy, and another, in terms of functional derivatives Eqn.72, and we obtain,

$$S_{11'}^{(H)}(t,t'') = \frac{1}{i}\frac{1}{\Gamma_{11'}}\delta(t-t'') + \left\{\frac{1}{i} [\mathcal{P}_{12}(t^+) + \bar{R}_{12}(t^+)]V_{23} - \frac{1}{i} V_{21}[\bar{P}_{14}(t^-) + \bar{R}^{c}_{14}((t^-)]\tau_{23}]\mathcal{G}_{31'}(t,t')\right\}G_{11}^{-1}((t',t'').$$ (76)

**A. The Hubbard-I approximation.**

The Hubbard-I approximation is obtained if we put all the functional derivatives equal to zero, $\bar{R}\mathcal{G} = 0$, which results in

$$S_{11'}^{(H)}(t,t'') = \Sigma_{11'}^{(H)}(t,t'') = \frac{1}{i}\frac{1}{\Gamma_{11'}}\delta(t-t'')\left\{\frac{1}{i} [\mathcal{P}_{12}(t^+)V_{21'} - V_{24} \bar{P}_{14}(t^-)\tau_{21'}]\right\}. $$ (77)
Since this term does not contain the factor $G^{-1}$, the $S$-self-operator here can be interpreted also as self-energy (denoted as $\Sigma$). If this expression will be used for a system in thermodynamical equilibrium and far from a phase transition to a state with intermediate valence, Hubbard’s arguments can be applied, namely, that instead of fully self consistent calculation of population numbers one can use just the atomic-like solution for them, $\mathcal{P}_{12}(t^+_1) \approx \mathcal{P}_{12}^{(0)}(t^+_1)$. Note that by putting functional derivatives of the GF equal to zero, we automatically neglect all the graphs, which renormalize the population numbers. Thus, this is the lowest possible approximation. In the equilibrium state external fields $\mathcal{U} = 0$. Therefore, all non-diagonal population numbers $\mathcal{P}_{14}^{\eta \eta'} = 0$. Then the corners $\langle Tcc \rangle$, $\langle TXX \rangle$ of the full matrix of GF give zeroes and it is sufficient to consider only the sub-block with $\eta = c, X$ and $\eta' = c^\dagger, X^\dagger$.

Then the expression

$$\Sigma^{(H)}_{13}(t_1, t_3) \big|_{\mathcal{U}=0} = \frac{1}{i} \delta(t_1^+ - t_3)[\mathcal{P}_{13}^R + \mathcal{P}_{12}(t^+_1)V_{23}],$$

(78)

gives the following system of equations in the supermatrix form,

$$i[D^0_{cc}(t)]^{-1}_{jL,j_1L_1} - \Theta_{jL,j_2c} \hat{W}^*_\nu_{j_2c,j_1L_1} - w_{jL,j_1b} - \Theta_{jL,j_2c} \tilde{t}^b_{j_1j_1} \quad \times$$

$$- \tilde{w}^b_{j_1j_1L_1} \quad i[D^0_{XX}(t)]^{-1}_{j_1a,j_1L_1} - \tilde{t}^{ab}_{j_1j_1}$$

$$= \begin{pmatrix}
G_{j_1L_1,j',L'}(t - t') \quad G_{j_1L_1,j'a}(t - t') \\
G_{j_2b,j',L'}(t - t') \quad G_{j_2b,j'a}(t - t')
\end{pmatrix}$$

$$i\delta(t - t') \begin{pmatrix}
O^{-1}_{jL,j'L'} \quad \Theta_{jL,j'\nu} P^{ba'}_{\nu} \\
P_{j}^{ab} \bar{\Theta}_{jB,j'\nu} \quad \delta_{jj'} P_{j}^{a'b'}
\end{pmatrix}$$

(79)

The Latin letters $D$ are used for $cc$- and $XX$-components of the pseudolocators, whereas their inverse pseudolocators here are the following differential operators:

$$i[D^0_{cc}(t)]^{-1}_{jL,j'L'} \equiv \delta_{jj'} \delta_{LL'} i \partial_t - (O^{-1}H)_{jL,j'L'},$$

(80)

$$i[D^0_{XX}(t)]^{-1}_{j\alpha,j'b} \equiv \delta_{jj'} \delta_{ab} (i \partial_t - \Delta_a),$$

(81)

and the interactions which are renormalized by (convoluted with) the population numbers, are denoted by a tilde,
Finally, the $\Theta$-matrix is:

$$\Theta_{jL,j'}^{c} \equiv O_{jL,j'M}^{-1}(f_{M})^{c}, \bar{\Theta}_{jM,j'L}^{c} \equiv (f_{M}^{\dagger})^{\dagger}O_{jM,j'L}^{-1}. \quad (83)$$

Thus, the new element, which appears in our Eqs.82 compared to normal LDA-based calculation, is that both effective mixing and hopping matrix elements are decreased by the population numbers of many-electron states of the ion, since usually they are less than one. The latter is always the case if mixing of localized and delocalized electrons is not equal to zero. It is worth noticing that any further corrections to the population numbers, which do not change their locality and do not introduce an energy dependence, do not change the structure of these equations. The approximation, where these population numbers are dressed, but still do not depend on energy, we will call ”Hubbard-I”approximation. The corresponding self-energy is shown in Fig.1.

Let us emphasize what is achieved for a moment by this construction, i.e., which are the new features of our ”Hubbard-I” equations, which differ them from the standard LDA ones. First, we passed from the ground-state description of the system to the statistical one, therefore, some of thermodynamical properties can be calculated.

Second, we know now where the $f$-level is situated with respect to the Fermi energy and other bands just by construction of the Hamiltonian. This is important for example, for calculation of contribution of mixing interaction into effective interaction of conduction and localized electrons.

Third, in spite of the allowance of mixing interaction between localized and delocalized electrons the atomic-like Hund’s rules can be taken into account (already at the level of constructing of the zero Hamiltonian ).

Fourth, the possible degeneracy of many-electron states involved is taken into account by the form (25) of the population numbers.

Fifth, since the single-site contributions from the Coulomb and exchange interactions are included by construction into the energies of many-electron states $E_{\Gamma}$, the calculation of
an effective exchange interaction between the angular momenta (also, interaction between quadrupole momenta, ..., etc.) of different atoms does not require special care, which is necessary within the standard LDA model for heavy rare earths\textsuperscript{22}.

Finally, the interaction of quasilocalized electrons with itselfes (self-interaction correction) is taken into account by construction.

It is obvious from a physical point of view, however, that the approximation described above has very serious drawbacks. If some of $f$-ions has $n$ $f$-electrons in the ground state, the state with $n + 1$ electrons belongs to the excited ones and usually is separated by such a large energy gap from the ground state, that the energy difference $\Delta_{\Gamma, \Gamma'}^{n+1,n} \equiv E_{\Gamma}^{(n+1)} - E_{\Gamma'}^{(n)}$ exceeds the Fermi energy and lies in the energy interval of the delocalized part of the spectrum of single-electron excitations. Corresponding excitations unavoidably should become delocalized. Therefore, part of the spectral weight should be moved into this energy region and the renormalization of the population numbers (combination of which describes in this approximation also the spectral weights) and, also, the energies of the transitions $\Delta_{\Gamma, \Gamma'}^{n+1,n}$, should contain the contribution from this delocalized part of spectrum. The Hubbard-I approximation misses it. These corrections arise only in higher approximations. The other drawback of this approximation is that the atomic-like $f$-levels remain non-renormalized by the interaction of the $f$-ion with surrounding medium. This shift should arise due to admixture of the wave functions of neighboring sites to the one of the reference site and interactions of $f$-electrons with bosonic excitations (analogously to the Lamb shift in quantum electrodynamics). All these effects can be taken into account via the corrections to the self-energy and we turn now to the formulation of this part of theory.

B. Vertexes and equation for self-operator in terms of vertex.

In order to obtain the next corrections we insert the GF, $\mathcal{G}_{36}$, in the form of Eqn.75 into the expression for the self-operator, Eqn.76. The differential operators $\hat{R}$ acting on the GF $\mathcal{G}$ gives,
\[
\hat{R}_{12}(t_1)\mathcal{G}_{31'}(t, t') = \hat{R}_{12}(t_1)[\mathcal{D}_{36}(t, t')\mathcal{P}_{61'}(t')] = \\
[\hat{R}_{12}(t_1)\mathcal{D}_{36}(t, t')]\mathcal{P}_{61'}(t') + \mathcal{D}_{36}(t, t')[\hat{R}_{12}(t_1)\mathcal{P}_{61'}(t')] = \\
-\mathcal{D}_{39}(t, t_9)[\hat{R}_{12}(t_1)\mathcal{D}_{98}^{-1}(t_9, t_8)]\mathcal{G}_{81'}(t_8, t') + \\
\mathcal{D}_{36}(t, t')[\hat{R}_{12}(t_1)\mathcal{P}_{61'}(t')]
\]

(84)

where the trick\(^\text{[9]}\)

\[
\hat{R}_{12}(t_1)[\mathcal{D}_{36}^{-1}(t_3, t_6)\mathcal{D}_{67}(t_6, t_7)] = 0 \Rightarrow \\
\hat{R}_{12}(t_1)\mathcal{D}_{36}(t_3, t_6) = -\mathcal{D}_{39}(t_3, t_9)[\hat{R}_{12}(t_1)\mathcal{D}_{98}^{-1}(t_9, t_8)]\mathcal{D}_{86}(t_8, t_6),
\]

(85)

has been used. Having in mind that the \(\hat{R}\)-operator is equal to zero when both indexes run over \(c\)-electrons, we restore its definition via the matrices \(\alpha\) for the \(\hat{R}^l\) - and \(\beta\) for the \(\hat{R}^r\)-operators and introduce the vertexes in a standard way, namely, as functional derivative of the inverse GF with respect to external field,

\[
\hat{R}^l_{12}(t_1^+) \quad \mathcal{D}_{78}^{-1}(t_7, t_8) \equiv \lim_{t_4 \to t_1^+} \alpha_{12,4b}^{\eta_7} \frac{\delta}{\delta U^{\eta_7}_{j_3}(t_4)} \mathcal{D}_{98}^{-1}(t_9, t_8) \\
\equiv \lim_{t_4 \to t_1^+} \alpha_{12,4b}^{\eta_7} \Gamma_{98,4b}^{l}(t_9, t_8; t_4) \equiv \alpha_{12,4b}^{\eta_7} \Gamma_{78,4b}^{l}(t_7, t_8; t_1^+),
\]

(86)

\[
\hat{R}^r_{12}(t_1^-) \quad \mathcal{D}_{78}^{-1}(t_7, t_8) \equiv \lim_{t_4 \to t_1^-} \beta_{12,4b}^{\eta_7} \frac{\delta}{\delta U^{\eta_7}_{j_3}(t_4)} \mathcal{D}_{98}^{-1}(t_9, t_8) \\
\equiv \lim_{t_4 \to t_1^-} \beta_{12,4b}^{\eta_7} \Gamma_{98,4b}^{r}(t_9, t_8; t_4) \equiv \beta_{12,4b}^{\eta_7} \Gamma_{78,4b}^{r}(t_7, t_8; t_1^-).
\]

(87)

It is worth noting that in our case the role of standard GF is played by the pseudolocators, and in this respect the introduced vertexes are indeed the standard ones. The new elements, which arise in the techniques for non-fermion operators, are the derivatives \(\hat{R}\mathcal{P}\). They can be written via the correlation functions of Bose-like transitions (see Eq.95 below) and we will discuss them a little later. The other new element (compared to the standard case) is that the vertexes which enter the equations in the ” left” and ”right” limits. The origin of this difference is seen from the definitions of the operators \(\hat{R}^l_{12}(t_1^+)\) and \(\hat{R}^r_{12}(t_1^-)\); the vertex in the left limit arises in the usual technique too, while the one in the right limit arises from transitions which involve creation or destruction of two particles on one site simultaneously.
This process is described in the equations of motion by the anticommutator \( \{ \eta_1, \eta_2 \} \), which is equal to zero in the case of usual fermions, but is not in the case of two-electron intra-atomic transitions.

Using these expressions we obtain the following equation for the self-operator,

\[
S_{1''}(t, t'') = \Sigma_{1''}(t, t'') - \frac{1}{i} V_{23} D_{30}(t, t_9) \alpha_{12,5_b}^{\eta_1,5_b} \Gamma_{91,5_b}(t_9, t''; t') + \\
\frac{1}{i} V_{24} \tau_{23} D_{30}(t, t_9) \beta_{14,5_b}^{\eta_1,5_b} \Gamma_{91,5_b}(t_9, t''; t') + \\
( - \frac{1}{i} V_{23} D_{30}(t, t') [\hat{R}^{1'}_{12}(t') P_{61'}(t')]) - \\
\frac{1}{i} V_{24} \tau_{23} D_{30}(t, t') [\hat{R}^{1'}_{14}(t') P_{61'}(t')] G^{-1}_{1''}(t', t'').
\] (88)

Thus, structurally the self-operator can be separated into the sum of a few terms

\[
S = S_H + S_1 + S_P, \quad S_H = \Sigma_H; \quad S_1 = \Sigma_1; \quad \Sigma_1 = \Sigma_L + \Sigma_R,
\] (89)

where \( \Sigma_L \) and \( \Sigma_R \) are the terms which contain left \((\sim \alpha)\) and right \((\beta)\) vertexes and are genius self-energies \( \Sigma \) \((i.e.,\) the graphs, which cannot be separated into two non-linked graphs but cutting one line of \( D \)-function), while \( S_P \), the contribution, proportional to \( G^{-1} \), contains derivatives of the population numbers and renormalizes end-factors. Let us also consider the corrections to \( \Sigma_1 \). First we need the bare vertex. The definition of it arises if we replace the full inverse pseudolocator in Eqns.86-87 by the bare one, \( D^{-1} \rightarrow D_0^{-1} \). Since \( \hat{R}(t) D_0^{-1} = \alpha (\delta D_0^{-1}/\delta U) = -\alpha (\delta A/\delta U) \), and a similar relation holds for \( \hat{R}''(t) D \), the number of different bare vertexes is determined by the number of different combinations of external fields \( A \), (Appendix D, Eqs.1-8). From the definition of the self-operator \( D^{-1} = D_0^{-1} - S \) we see that the exact total vertex being derivatives of the self-operator with respect to external fields, can be rewritten in the form of a sum of the bare vertex \( \gamma \) and corrections,

\[
\Gamma_{98,5_b}(t_9, t_8; t_5) = \gamma_{98,5_b}(t_9, t_8; t_5) - \frac{\delta S_{98}(t_9, t_8)}{\delta U_{5_b}(t_5)},
\] (90)

\[
\gamma_{98,5_b}(t_9, t_8; t_5) = -\delta (t_9 - t_8) \frac{\delta A_{98}(t_8)}{\delta U_{5_b}(t_5)}.
\] (91)
These relations are useful for obtaining subsequent corrections to the vertex, substituting into Eqs.86,87 approximate expressions instead of the full self-operator. We will return to it a bit later. Before that, let us rewrite with the help of Eqs. 76,88 the equation for the full GF in a form which clarifies the physical meaning of different terms in the self-operator (Eqn.89). Using the pseudolocator in the Hubbard-I approximation, \( D^{-1}_H = D^{-1}_0 - \Sigma_H \), we find,

\[
\{(D^H(t,t''))^{-1}_{11'} - \frac{1}{i} D_{39}(t,t_9)[V_{23} \alpha_{12,5b} \Gamma_{91''5b}(t_9, t''; t^+)} - \\
- \frac{1}{i} V_{24} \tau_{23} \beta_{14,5b} \Gamma_{91''5b}(t_9, t''; t^-)] \} \mathcal{G}_{1''1'}(t'', t') = \\
\mathcal{P}_{11'}(t, t') + \Delta \mathcal{P}_{11'}(t, t'),
\]

where the renormalization of the population numbers is given by the following expression:

\[
\Delta \mathcal{P}_{11'}(t, t') \equiv - \frac{1}{i} V_{23} D_{36}(t, t')[\hat{R}_{12}^i(t^+) \mathcal{P}_{61'}(t')] + \\
\frac{1}{i} V_{24} \tau_{23} D_{36}(t, t')[\hat{R}_{14}^r(t^-) \mathcal{P}_{61'}(t')],
\]

Thus, we see that the self-operator can be represented as \( S = \Sigma + \Delta P \cdot G^{-1} \) what allows to separate the graphs to the ones which renormalize the pseudolocator \( D \) and are the contributions to the self-energy, and the ones which renormalize the end-factor \( \Delta P \). Let us turn now to the Bose-type of GFs. In order to obtain the equation for these GFs, we will use again the short-index notations \( 1_b \equiv (j_1 \xi_1) \) and rewrite the equation for the boson-like GF in terms of vertex, Eqn.86 (we have to use once more time the Kadanoff and Baym’s trick-Eqn.85). Then we obtain,

\[
\begin{align*}
[L^0(t_1, t_2)]_{1b,2b}^{-1} K_{2b,1b'}(t_2, t_1') &= \delta(t_1 - t_1') P_{b1b'}(t_1') + \\
\lim_{t_2 \to t_1 + 0+} \frac{1}{i} V_{1,2}^{1b} \langle TZ_{1b'}(t') \rangle_a G_{21}(t_1, t_2) + \\
\lim_{t_2 \to t_1 + 0} V_{1,2}^{1b} \frac{1}{i} D_{24}(t_1, t_4) \Gamma_{45,1b'}(t_4, t_5; t_1') G_{51}(t_5, t_2) - \\
D_{23}(t_1, t_2) \bar{\alpha}_{31;3b'}[K_{3b,1b'}(t_1', t_2) - \langle TZ_{1b'}(t_1') \rangle_a \langle TZ_{3b}(t_2) \rangle_a].
\end{align*}
\]

Here we have used the definition of \( P_{31'}(t_2) \), Eqs.60 and 61 and represented the derivative \( \delta P/\delta U \) in the last term of this equation in the form,
\[ \frac{\partial \alpha^{n\ell}_{31';3b}}{\partial U_{1b}'(t_1')} \delta P_{3b}(t_2) = \frac{1}{\ell} \left[ K_{3b;1b}'(t_1', t_2) - \langle TZ_{1b}'(t_1') \rangle u \langle TZ_{3b}(t_2) \rangle u \right]. \] (95)

This completes the derivation of the exact equation for the boson-like GFs. Eqs.94,95 should be used also in Eqs.84,88 and 90 for calculation of \( \hat{R}^d P \) and \( \hat{R}^r P \).

The way of deriving different approximations for the boson type of GFs is quite similar to the one used above for the fermion-like excitations. First, of course, we have to define the zero-order GF, putting \( V = 0 \) in Eq.94, which gives

\[ K_{2b;1b}'(t_2, t_1') = L_{2b;3b}(t_2, t_1') P_{3b;1b}'(t_1'). \] (96)

Then an analogue of the Hubbard-I approximation for fermion-like transitions arises if we put in Eq.94 the vertex \( \Gamma = 0 \). As seen from the Hamiltonian, within the Hubbard-Anderson model, the only way a renormalization of the boson-like GFs arises is due to mixing interaction and hopping, therefore, it requires knowledge of the electron GF. The latter creates fields which shift the energies of the bosonic transitions.

**C. Mean field approximation and self-consistent equation for Hubbard \( U \).**

As seen from Eq.92, the part of the self-consistency which does not involve the effects of \( S_P \), can be provided in the usual way: a choice of certain approximation for the vertexes, \( \Gamma \rightarrow \Gamma^{(appr)} \), leads to a corresponding expression for the self-energy via Eq.(88), while the GFs entering the \( \Gamma^{(appr)} \) (if \( \Gamma \neq \gamma \)) contain the same \( \Sigma \) and \( \Gamma^{(appr)} \). According to this scheme the simplest approximation which is beyond the Hubbard-I approximation, should contain the vertex. It arises if we neglect the terms \( \hat{R} \Sigma \) in the equations for \( \Gamma \), i.e., \( \Gamma \rightarrow \gamma \). Since the \( ff \)-part of \( D_0^{-1} \) is purely local, and the bare vertex does not depend on energy, the diagonal parts of the loops

\[ \Sigma_{11''}(t, t'') = -\frac{1}{i} V_{23} D_{39}(t, t_9) \alpha^{n\ell}_{12,5b}(t_9, t''; t^+) + \frac{1}{i} V_{24} t_{23} D_{39}(t, t_9) \beta^{n\ell}_{14,5b}(t_9, t''; t^-) \] (97)

renormalize the centers of \( f \)-bands.
Indeed, since we assumed that $f$-functions, belonging to different sites do not overlap with each other, $O_{i,L} = f_{i,j,L'} = 0$, we see that the energy $\Delta_a$ of the transition $a = [\Gamma_n, \Gamma_{n+1}]$ is shifted by $\delta \Sigma_{\text{loop}}$; if we neglect the non-diagonal corrections, we find the following equation:

$$\Delta_a^* = \Delta_a + (\Sigma_{\text{loop}})_{1=(i,\tilde{a}), 2=(i,\tilde{a})} \equiv \Delta_a + \delta \Delta_a(\Delta_a^*). \tag{98}$$

This is self-consistent equation for transition energy; renormalization comes from hopping and mixing interaction. If we take Hubbard’s estimate for $E_G$, $E_G = \varepsilon_0^n + \frac{1}{2}Un(n-1)$, then the energies of the transitions $\Delta_2^0 = \Delta_{\tilde{a}} = [\Gamma_{n+1}, \Gamma_n] = E_{\Gamma_{n+1}} - E_{\Gamma_n} \approx U/2$; the lower transition $\Delta_1^0 = \Delta_{\tilde{a}} = [\Gamma_n, \Gamma_{n-1}] \approx U/2$ too. Here we used the Hubbard’s estimate for $\varepsilon_f$: the main contribution to this energy comes from attraction to nucleous, which provides localization of certain number $n_0$ of $f$-electrons. Therefore, $dE_n/dn = 0$ gives $\varepsilon_f^0 = -(n_0 - \frac{1}{2})U$. Correspondently, a fermion $ff$-GF has two poles. The lower one is located near energy of lower transition $\Delta_1^0$ and the upper one $\Delta_2^0$; the Hubbard bands are developed near these energies. The shifts of $\Delta_i^0$ ($i=1,2$) due to hopping and mixing can be roughly estimated as

$$\delta \Delta_i \approx \sum_p \tilde{t}_i^{\text{hop}}(p) f(E_p^i) i + \sum_{p,\lambda} V_{\lambda}^{a_i}(p) V_{\lambda}^{a_i}(p) \frac{\Delta_i^*}{\varepsilon_{\lambda p}} f(E_p^i), \quad i = 1, 2. \tag{99}$$

Here $\tilde{t}_i^{\text{hop}}(p)$ is an effective hopping, containing all chain ($\sim$ Hubbard-I approximation) contributions. However, at large enough $\Delta$ main contribution comes from the second order ($\sim t^2/\Delta \sim t^2/U$).

It is also easy to see that the equation $\Delta^* = \Delta + \delta \Delta(\Delta^*)$ can have two solutions, one of which is located near Fermi energy, which is often called as "Kondo resonance". These two equations show that, contrary to the $s$-band Hubbard model, one can expect that in reality the renormalizations of $\Delta_1^0$ and $\Delta_2^0$ should be quite different, at least, for rare earth ions: on the one hand, hopping and mixing are strongly suppressed in the region of energies $\omega \sim \Delta_1^0$ since this energy is very deep under Fermi surface and even below the bottoms of conduction bands; on the other hand, in the region of energies $\omega \sim \Delta_2^0$ hopping and mixing should be much stronger, therefore, in the region of energies in vicinity of Fermi level the mechanism described by Eq.99 can be much more effective. It is clear, however, that this mechanism
is not able to provide strong reduction of the bare Hubbard repulsion $\Delta_2^0 - \Delta_1^0 \simeq U$ from 20eV to $5 \div 7$eV (the latter is the value usually obtained within LDA-based calculations). Therefore, other, stronger contributions, should be generated by full Hamiltonian. Nevertheless, it worth to note that the non-diagonal matrix elements of hopping, $t^{\lambda \mu}(f^\dagger_\lambda)^a(f_\lambda)^b$ and effective hopping via mixing, $\sim [V^*_\lambda(p)V^h_\lambda(p)/(\omega - \varepsilon_{\lambda p})](1 - \delta_{ab})$, split the Eq.99 to the system of equations.

At last, its $cf$-parts renormalize the mixing interaction. The self-energy which includes the Hubbard-I and the loop correction Eqs.(97,98), still does not depend on energy. Since this approximation is also beyond the Hubbard-I approximation, we will call it mean field approximation (MFA). Similar approximation for multiple-orbital Hubbard model but for the simpler case of orthogonal basis set has been considered earlier\textsuperscript{45}. The fact, that the equations for fermion-like GFs always contain vertexes in combination with the matrices $\alpha$ and $\beta$ allows to use a shorter graphical notation: the sums $\alpha \cdot \gamma$ and $\beta \cdot \gamma$ can be represented as four-leg vertexes, as shown in Fig.2. Then, in this graphical language the loop correction, Eq.97, acquires the form shown in Fig.3.

D. Further corrections to vertexes and self operator.

In order to obtain the second-order corrections to vertexes and self-energy we insert $\delta \Sigma = \delta \Sigma^{\text{loop}}$, Eq.97, into the definition of the vertexes Eqs.86,87,90,91. Since neither the interaction $V$, nor the matrix $\tau$ depend on the external fields, only pseudolocators entering the $\Sigma^{(1)}$ give non-zero contribution when we calculate the functional derivatives $\hat{R}\Sigma$. Therefore, we can construct the higher-order corrections simply by formulation of the rule of differentiation of the pseudolocator lines. This rule is displayed in Fig.4. Applying it to the graphs of the $\Sigma^{(1)}$, shown in Fig.3, we obtain the desired corrections of second order to vertexes (displayed in Fig.5). Then, inserting these corrections to the definition of the self-operator via the vertex, Eq.88, we obtain the corresponding second-order corrections to the self-operator. The graphs for these corrections are shown in Fig.6. The corrections to the vertex in Fig.5
describe contributions of electron-hole excitations to the kinematic interactions, which arises due to strong correlations and are caused by mixing and hopping. Note, that there are also other, formal, difference with the standard case: instead of pure GF one of the shoulders of the electron-hole loop contains the product of the line of interaction $V$ (wiggle line) and the pseudolocator.

E. The screening

The next obvious step is to take into account the screening effects. The lowest approximation is an analogue of the standard random-phase approximation, used in the theory of normal metals. In order to avoid possible confusion, we remind the reader that here again it renormalizes not the Coulomb interaction but only mixing and $ff$-hopping. One way to construct it would be to solve the integral equation for vertex, generating the series of "electron-hole" loops (see Fig.4) and insert the solution of this equation, i.e., corrected vertex, into self-energy for pseudolocator; then to derive similar corrections to the population numbers (r.h.s. of Eq.92 for the GF). The equivalent, but shorter way, which automatically renormalizes the interaction $V$ in all corrections, is to make an exact transformation of the shift in the external field of Eqs. 40-43,52,92,94, introducing the description in terms of effective fields, $\Phi = A + \Sigma^{(\text{loop})}$. The quasifermion GFs depend on the external field $\mathcal{U}$ only via the "gauge" field $A_{12}(t) \equiv \nu_{12}^{i} \mathcal{U}_{ib}(t)$, where the matrices $\nu$ are listed in Appendix D. Therefore, we can express equations for these GFs in terms of derivatives $\delta/\delta A^{\text{eff}}$, schematically, we have

$$V \frac{\delta}{\delta \mathcal{U}_{ib}(t)} = (V \frac{\Phi_{12}(t)}{\delta \mathcal{U}_{ib}(t)}) \frac{\delta}{\Phi_{12}(t)} = [V(\nu_{12}^{i} + \frac{\delta \Sigma^{(\text{loop})}}{\delta \mathcal{U}_{ib}(t)}(t_1))] \frac{\delta}{\Phi_{12}(t)}.$$  \hspace{1cm} (100)

Let us now perform this calculation. First we have to separate out the loop contribution (97) of the self-energy in the equation for GF (Eqn.92). This one-loop correction contains zero vertex $\gamma$; self-consistency requires that the full GF, which enters the loop, should contain the same self-energy, which is taken into account in the equation for GF. Taking into account that
\[ \gamma_{91',5b}(t_9, t''; t) = -\delta(t_9 - t'')\delta(t_9 - t)\nu_{91',5}^{5b}, \quad (101) \]

and including the self-energy correction \( \Sigma^{(\text{loop})} \) into the effective field,

\[
\Phi_{11'}(t, t'') \equiv A_{11'}(t, t'') + \frac{1}{t} \alpha_{12;5b}^m V_{23} D_{39}(t^-) \nu_{91',5}^{5b} \delta(t^+ - t'') + \frac{1}{t} \beta_{12;5b}^m V_{24} \tau_{23} D_{39}(t^-) \nu_{91',5}^{5b} \delta(t^- - t''), \quad (102) \]

we find, that the factor \( Y_{11',2b}(t, t') \equiv \delta \Phi_{11'}(t)/\delta U_{2b}(t') \) which renormalizes the interaction, should satisfy the following equation,

\[
Y_{11',2b}(t, t') = \nu_{91',5}^{5b} [\delta_{91} \delta_{25b} \delta(t - t') - D_{3,10}(t, t_0) \delta D_{10,11}^{-1}(t_0, t_{11})/\delta U_{2b}(t')] \times \{ \alpha_{12;5b}^m V_{23} D_{11,9}(t_{11}, t^+) \delta(t^+ - t'') + \beta_{14;5b}^m V_{24} \tau_{23} D_{11,9}(t_{11}, t^-) \delta(t^- - t'') \}. \quad (103) \]

Eq.103 contains full pseudolocator \( D \).

\[1. \text{Fermi-liquid-like random phase approximation (RPA)}\]

If we substitute into Eq.103 the bare vertex \( \gamma = \delta D_{0l}^{-1}/\delta U_{1b} \) instead of the full vertex \( \Gamma = \delta D^{-1}/\delta U_{1b} \), we obtain only the first correction to \( Y \). In order to obtain a closed equation for \( Y \), we have to take into account in \( D \) the same correction to \( \Sigma \), namely, \( \Sigma^{(\text{loop})} \). Since

\[
\delta D_{0l}^{-1}/\delta U_{1b} = -\delta \Phi/\delta U_{1b} = -Y, \quad (104) \]

with \( D_{0l}^{-1} \equiv D_{0l}^{-1} - \Sigma^{(\text{loop})} \) (\( \delta \)-functions are omitted) we obtain the desired equation,

\[
Y_{11',2b}(t, t') = \nu_{91',5}^{5b} [\delta_{91} \delta_{25b} \delta(t - t') - D_{3,10}(t, t_0) Y_{10,11,2b}(t_{10}, t_1) \times \{ \alpha_{12;5b}^m V_{23} D_{11,9}(t_{11}, t^+) \delta(t^+ - t'') + \beta_{14;5b}^m V_{24} \tau_{23} D_{11,9}(t_{11}, t^-) \delta(t^- - t'') \}]. \quad (105) \]

Note that the complex structure of coupling of the Fermi-like excitations to the Bose-like ones makes the screening matrix dependent on three indices.
2. Full equation for the GF in terms of RPA GF

Now let us write down the self-energy part of the self-operator in the l.h.s. of Eq.112, which can be named $\Sigma_D$ (the index $D$ here emphasizes that it relates only to the pseudolocator $D$), in the form: $\Sigma_D = \Sigma^H + \Sigma^{\text{loop}} + \Sigma^{\text{rest}}$. The effective field in these terms is $\Phi = A + \Sigma^{\text{loop}}$. Note that since $\Sigma^H$ is not local, it cannot be included into effective field $\Phi$. Then, the vertex $\Gamma$, defined by Eqs. (86), (87) and (90) can be expressed in terms of $Y$ as follows,

$$\Gamma_{91',5b}(t_9,t'';t_4) = -[Y_{91',5b}(t_9,t_4)\delta(t'' - t_9) + \frac{\delta\Sigma^{\text{rest}}_{91'}(t_9,t'')}{\delta\Phi_{67}(t_6)}Y_{67,5b}(t_6,t_4)]. \quad (106)$$

With the help of this expression for the vertex we can represent the equation for the full GF (92) in a form which does not contain the non-screened interaction,

$$\{D^{-1}_{RPA,11'}(t,t'') - \frac{1}{i}D_{3,9}(t,t_9)[\alpha_{12,5b}^{\text{m}1}\frac{\delta\Sigma^{\text{rest}}_{91'}(t_9,t'')}{\delta\Phi_{67}(t_6)}V_{23}Y_{67,5b}(t_6,t_+)} - \beta_{14,5b}^{\text{m}1}\frac{\delta\Sigma^{\text{rest}}_{91'}(t_9,t'')}{\delta\Phi_{67}(t_6)}V_{24}Y_{67,5b}(t_6,t_-)]\}G_{1'1'}(t'',t') = P_{11'}(1,1') + \Delta P_{11'}(1,1'), \quad (107)$$

where the derivatives $\delta/\delta U$ in the formula (93) for $\Delta P$ are also rewritten in the form $\delta/\delta U = Y \frac{\delta}{\delta \Phi}$. At last, the equation for the pseudolocator $D_{RPA}$ becomes,

$$[\delta(t,t'')\delta_{12} V(t',t'')] + \frac{1}{i}V_{23}G_{12,5b}^{\text{m}1}D_{3,9}^{\text{MF}}A(t,t'')Y_{91',5b}(t_9,t_+) - \frac{1}{i}V_{24}G_{14,5b}^{\text{m}1}D_{3,9}^{\text{MF}}A(t,t'')Y_{91',5b}(t_9,t_-)]D_{RPA,24}(t'',t') = \delta_{24}\delta(t'' - t'). \quad (108)$$

The role played by $Y$ in the strong-coupling theory is analogous to the one played by dielectric function in the weak-coupling theory of Coulomb systems: it describes the screening of the interaction $V_{12}$.

V. COULOMB INTERACTION

The detailed consideration of the Coulomb interaction is given in next paper, here show the technical idea of description and emphasize the new elements arising within this approach.
Full Coulomb interaction have been written in $X$-representation as follows:

$$H_{\text{coul}} = \sum v_{1234}(c_1^\dagger + (f_1^\dagger)^\alpha_1 X_{1}^{\alpha_1})(c_2^\dagger + (f_2^\dagger)^\alpha_2 X_{2}^{\alpha_2})(c_3 + (f_3)^\alpha_3 X_{3}^{\alpha_3})(c_4 + (f_4)^\alpha_4 X_{4}^{\alpha_4}). \quad (109)$$

The single-site terms $v f^\dagger f^\dagger f f$ have been transformed into $\sum E_{\Gamma} h_{\Gamma}$; the terms which contain three single-site $f$-operator and one operator of conduction electron are included to mixing interaction $V c^\dagger X + h.c.$; the terms of the kind $v(f^\dagger f^\dagger f)_{jj'} (1 - \delta_{jj'})$ are included into Hubbard’s hopping Hamiltonian. Note that in case if some selection rules happen to be valid for the single-particle matrix elements of hopping and mixing interaction, the effective matrix elements have different selection rules due to presence of Coulomb terms in it. All the other terms should be considered. Remind that due to large strength of on-site interaction we are not allowed to decouple the operators belonging to the same site. Thus, if these $f$-operators are not neighbors in the Hamiltonian, we have to move (using rules for anti commutations) them to each other and then either to transform the $f$-product into Hubbard operator(s) or to transform each $f$-operator into $X$-operator and multiply them. This procedure also helps to clarify a physical meaning of corresponding terms. The number of different terms in the Hamiltonian is large and we are not able to give here all formulas. Besides, a degree of importance of different terms is material- and scenario- dependent. Thus, we will consider here few terms in order to show how the developed above perturbation theory is to be modified in order to include Coulomb interaction between different sites (the description of the Coulomb intersite interaction within slave-boson technique has been considered earlier in Ref.3).

Let us start with the terms, which describe simultaneous ”hopping” of two electrons from one site to another:

$$H_1^C = \sum v_{jij'j''}(f_1^\dagger f_2^\dagger)(f_3 f_4)C_j^C Z_j^{\xi} Z_j'^{\xi} \equiv \sum C_j^C Z_j^{\xi} Z_j'^{\xi}. \quad (110)$$

One can expect that this term can be neglected in the lowest approximations since it involves large-energy transition (Hubbard $U$ in denominator): although $[X^a, Z^b]$ gives $X^b$ in equation of motion remaining operator $Z^a$ requires $Z^b$ in order to obtain non-zero result; the GF
$\langle T Z^n Z^0 \rangle$ gives makes the contribution small. The reason why these processes have to be considered is that there are high-order processes (like assisted spin-flips) which contain in denominator small difference of these large energies.

The terms

$$
H^C_1 = \sum [v_{j\mu_1j'\mu_2j'\mu_3j'\mu_4} (f_{\mu_1} \ f_{\mu_2}) \xi (f_{\mu_3} \ f_{\mu_4}) \xi' Z^C_j Z^C_{j'} \equiv \sum C_{j,j'}^C Z^C_j Z^C_{j'} . \tag{111}
$$

do not change number of $f$-electrons in ions. Part of these terms describe Coulomb screening of ions, part can be transformed into spin-spin, orbital-orbital interactions and so on. We will not consider particular terms from the sum over $\xi, \xi'$ here, however, note that on one hand, instead of one Heisenberg term $-I_{j,j'} J_J J_{j'}$ the expansion

$$
H_{\text{exch}} = - \sum I_{\alpha\beta\gamma} (j_1R)^{\alpha} (j_2R)^{\beta} (j_1J_2)^{\gamma} / R^{\alpha+\beta} . \tag{112}
$$

arises (with $\alpha + \gamma \leq 2l_1 + 1, \beta + \gamma \leq 2l_2 + 1, \alpha + \beta$ being odd and vector $R$ connecting ions); on the other hand, the different-site-exchange integrals $v_{j\mu_1j'\mu_2j'\mu_3j'\mu_4}$ are small due to small overlap of $f$-functions belonging to different sites, what makes the exchange-type of contributions from mixing and hopping visible on the background of positive direct exchange integrals and make non-ferromagnetic ordering (e.g., antiferromagnetism) possible. Now let us write down the terms, which are added into the equations of motion for the functions $\langle T c_n \eta \rangle_u$:

$$
\lim_{t'' \to t'} O_{n_1j\mu}^{-1} f_{\mu}^{\alpha \xi} C_{j,j'}^{\xi \xi'} \langle (Z^C_j(t'')) + i \frac{\delta}{\delta U^C_j(t''')} \langle (TX^C_{j'}(t)\eta^\dagger(t'))_u + \\
\lim_{t'' \to t'''} O_{n_1j'\mu}^{-1} f_{\mu}^{\alpha \xi} C_{j,j'}^{\xi \xi'} \langle (Z^C_{j'}(t''')) + i \frac{\delta}{\delta U^C_{j'}(t''')} \langle (TX^C_{j'}(t)\eta^\dagger(t'))_u. \tag{113}
$$

They contribute to the self-operator $\Sigma^c_X G^c X \eta$. The structure of this correction is similar to the term which comes in Eq.78 from hopping. Obviously, the Hartree corrections which is obtained by putting $\delta \langle T c \eta \rangle_u / \delta U = 0$, are the biggest terms, and of these terms the biggest one is the diagonal term, with $\xi = [\Gamma, \Gamma]$. Next terms, generated by $\delta \langle T c \eta \rangle_u / \delta U$, in lowest
approximation give the loop-corrections to the dielectric function and depend on the scenario under study.

Let us obtain now the contribution from this interaction to the equation for \( \langle TX^a\eta^\dagger \rangle_u \). Calculating corresponding commutator, we find quite similar result, namely, the term which should be added to \( \Sigma_{XX}G_{X\eta} \), has the form:

\[
\lim_{t'' \to t^-} \varepsilon_{b}^\alpha C_{j \ell j'}^{\delta \ell \delta} \delta_{n_j} \langle \mathcal{Z}_{j}(t'') \rangle + i \frac{\delta}{\delta U_{j}(t'')} \langle TX_{j}(t)\eta^\dagger(t') \rangle_u +
\]

\[
\lim_{t'' \to t^+} \varepsilon_{b'} C_{j \ell j'}^{\delta \ell \delta} \delta_{n_{j'}} \langle \mathcal{Z}_{j}(t'') \rangle + i \frac{\delta}{\delta U_{j}(t'')} \langle TX_{j'}(t)\eta^\dagger(t') \rangle_u. \tag{114}\]

This term has the structure similar to the one \( \sim t_{j,j'}^{bc} \) in Eq.40. In short notations we can write the two ones above as

\[
\lim_{t'' \to t^-} \varepsilon_{2}^{1b} C_{1a2b} \langle \mathcal{Z}_{2a}(t'') \rangle + i \frac{\delta}{\delta U_{2a}(t'')} \langle T\eta_2(t)\eta^\dagger(t') \rangle_u +
\]

\[
\lim_{t'' \to t^+} \varepsilon_{2}^{1b} C_{1a2b} \langle \mathcal{Z}_{1a}(t'') \rangle + i \frac{\delta}{\delta U_{1a}(t'')} \langle T\eta_2(t)\eta^\dagger(t') \rangle_u, \tag{115}\]

where notations are obvious from comparison with explicit form. Thus, these terms of Hamiltonian do not generate essentially new elements in the diagram technique. The Hartree term \( \varepsilon C\langle Z \rangle_u \) (the terms at \( \varepsilon C[ \delta/\delta U \rangle \langle TX^a\eta^\dagger \rangle_u = 0 \) describes the static screening of charges of neighboring ions, \( (Z - \rho_{\text{core}}) - \rho_f \). The non-spherical part of it is responsible also for the crystal field splitting of the states \( |\Gamma\rangle \). Usually this splitting is less important for the Fermi-like excitations than for Bose-like, where it can be seen directly in neutron scattering experiments. Sometimes, however, a scattering of conduction electrons on Bose-like excitations in crystal electric field can strongly renormalize effective electronic masses.\(^5\) The terms \( \sim \varepsilon C[ \delta/\delta U \rangle \langle TX^a\eta^\dagger \rangle_u \) describe effects of exchange and the dynamical screening from those \( f \)-bands which cross Fermi energy. The \( f \)-density in the close vicinity of Fermi level \( \varepsilon_F \) in normal materials is usually small and, therefore, these terms can be neglected. These contributions may play an important role in physics of the intermediate-valence (IV) compounds,\(^5\) and, also, of rare earth metals.\(^3\) In both latter cases the \( f \)-level can be situated just slightly above \( \varepsilon_F \). It can be important also in \( d - d \)-electron scattering in \( Fe, Co, Ni \) metals and their compounds.
Let us pass to a next term, \( v_{1234} a_1^\dagger a_2^\dagger a_3 a_4 \). Again we have to calculate the corrections which arise in equations of motion for GFs. Of course, all terms with two \( f \)-operators and two \( c \)-operators should be taken into account. Since they give similar contributions, for briefness we consider only one of them,

\[
v_{nL,j\mu j'n'L'}(c_{nL}^\dagger c_{n'L'}) (f_{j\mu j'n'}(t) f_{j'n'}(t'))^\xi \equiv C_{nL n'L'}^\xi \langle c_{nL}^\dagger c_{n'L'} \rangle Z_j^\xi .
\]  

(116)

Summation over transitions \( \xi \) includes both, the Coulomb interaction of the density-density type, and exchange interactions. Commutation of \( c \)-operator with this term generates in the equation for the GFs \( \langle T c_{iL}(t) \eta^\dagger (t') \rangle \) the GFs: \( \langle T c_{n_2 L_2}(t) Z_j^\xi (t) \eta^\dagger (t') \rangle_u \) and \( \langle T c_{n_1 L_1}^\dagger (t) c_{n_2 L_2}(t) X_j^b (t) \eta^\dagger (t') \rangle_u \). One can express them via functional derivatives of GFs as follows:

\[
\lim_{t'' \to t^-} (O^{-1})_{iL,n_1 L_1} C_{n_1 L_1 n_2 L_2}^{j\xi} \left[ (T Z_j^\xi (t''))_u + i \frac{\delta}{\delta U_j^\xi (t'')} \right] \langle T c_{n_2 L_2}(t) \eta^\dagger (t') \rangle_u + \\
\lim_{t'' \to t^+} (O^{-1})_{iL,j\mu j'n'L'} C_{n_1 L_1 n_2 L_2}^{j\xi} \left[ (T c_{n_1 L_1}^\dagger (t) c_{n_2 L_2}(t))_u + \\
i \frac{\delta}{\delta F_{n_1 L_1 n_2 L_2} (t'')} \right] \langle T X_j^b (t) \eta^\dagger (t') \rangle_u .
\]  

(117)

First line gives contribution to \( S_{cc} G_{cij} \), the Hartree term, \( \sim O^{-1} C \langle T Z \rangle \), describes a simple fact, that the conduction electron ”sees” screened by \( f \)-electrons ion’s charge, \( (Z - \rho_{core}) - \rho_f \), as well as with average angular moment if the phase under consideration has a long-range magnetic order. At zero external fields \( \langle T Z \rangle \rightarrow \langle h^\Gamma \rangle \equiv N_{\Gamma} \) and \( \langle T J_j \rangle \rightarrow \langle J_j^\eta \rangle \). Second line in this formula contains new element, \( \delta / \delta F \), describing creation of the conduction-band electron-hole pair (contribution to \( S_{cX} G_{X\eta} \)).

Let us turn now to the GFs \( \langle T X_j^\xi (t) \eta^\dagger (t') \rangle_u \). From equations of motion we find that the correction to right-hand side,

\[
C_{n_1 L_1 n_2 L_2}^{j\xi} \times \langle \delta G_{IV} \rangle_{n_1 L_1 n_2 L_2}^{j\xi,i}
\]  

(118)

involves quite complex GFs:

\[
\langle \delta G_{IV} \rangle_{n_1 L_1 n_2 L_2}^{j\xi,i} = (O^{-1})_{i\mu,n_1 L_1} (f_{i\mu}^\dagger \delta_{a^\xi_b}^a \langle T Z_j^\xi (t) c_{n_2 L_2}(t) Z_j^\xi (t) \eta^\dagger (t') \rangle_u - \\
- \langle T Z_j^\xi (t) c_{n_2 L_2}(t) Z_j^\xi (t) \eta^\dagger (t') \rangle_u)
\]

51
\[(O^{-1})_{n_2L_2;j^\mu j} \frac{\delta}{\delta \eta_i} \langle Tc_{n_1L_1}(t)Z^i_j(t)\eta^\dagger(t') \rangle_u + \]
\[\delta_{ij} \varepsilon^\xi_b \langle Tc_{n_1L_1}(t)c_{n_2L_2}(t)X^b(t)\eta^\dagger(t') \rangle_u. \quad (119)\]

The GFs in first two lines contain per two \(Z\)-operators, therefore, in our equations appears the new element, derivatives of second order:

\[
\langle TZ^i_j(t)c_{n_2L_2}(t)Z^\xi_j(t)\eta^\dagger(t') \rangle_u =
\lim_{t'' \rightarrow t^+} \left[ \langle TZ^i_j(t') \rangle_u + i \frac{\delta}{\delta U^i_j(t')} \right] \langle Tc_{n_2L_2}(t)Z^\xi_j(t)\eta^\dagger(t') \rangle_u =
\lim_{t'' \rightarrow t^-} \left[ \langle TZ^i_j(t') \rangle_u + i \frac{\delta}{\delta U^i_j(t')} \right] \times
\{ \lim_{t_3 \rightarrow t^-} \langle TZ^\xi_j(t_3) \rangle_u + i \frac{\delta}{\delta U^\xi_j(t_3)} \} \langle Tc_{n_2L_2}(t)\eta^\dagger(t') \rangle_u. \quad (120)\]

Thus, we’ve obtained the correction to \(\Sigma_{Xc}G_{c\eta}\). In the same fashion we find that

\[
\langle Tc_{n_1L_1}(t)Z^i_j(t)Z^\xi_j(t)\eta^\dagger(t') \rangle_u =
\lim_{t'' \rightarrow t^-} \left[ \langle TZ^\eta_j(t') \rangle_u + i \frac{\delta}{\delta U^\eta_j(t')} \right] \langle Tc_{n_1L_1}(t)Z^\xi_j(t)\eta^\dagger(t') \rangle_u =
\lim_{t'' \rightarrow t^-} \left[ \langle TZ^\eta_j(t') \rangle_u + i \frac{\delta}{\delta U^\eta_j(t')} \right] \times
\{ \lim_{t_3 \rightarrow t^-} \langle TZ^\xi_j(t_3) \rangle_u + i \frac{\delta}{\delta U^\xi_j(t_3)} \} \langle Tc_{n_1L_1}(t)\eta^\dagger(t') \rangle_u. \quad (121)\]

Note, that this term does not give corrections of mean-field type, of first order, \(\sim v_{n_1L_1n_2L_2}^{ij}\).

At last, the function \(\langle T(c^\dagger cX)\eta^\dagger \rangle_u\) can be written down as

\[
\langle Tc_{n_1L_1}(t)c_{n_2L_2}(t)X^b(t)\eta^\dagger(t') \rangle_u =
\lim_{t'' \rightarrow t^+} \left[ \langle Tc_{n_1L_1}(t')c_{n_2L_2}(t') \rangle_u + i \frac{\delta}{\delta F_{n_1L_1n_2L_2}(t''')} \right] \langle X^b(t)\eta^\dagger(t') \rangle_u
\]

and gives contribution to \(\Sigma_{XX}G_{XX}\).

The mean-field contribution from the last term, \(\delta\Delta^\text{Coul}_b \equiv v_{n_1L_1n_2L_2}^{ij} \langle Tc_{n_1L_1}c_{n_2L_2} \rangle_u^\eta_c \), should be added to the equation for effective energies of transitions \(\Delta_1^*\) and \(\Delta_2^*\) (see Eqs.98,99):

\[
\Delta_i^* = \Delta_i^0 + \Delta_i^\text{mixing} + \Delta_i^\text{hopping} + \Delta_i^\text{Coul}, \quad i = 1, 2. \quad (122)\]
As we discussed above, the correction $\Delta_{\text{mixing}}^1 + \Delta_{\text{hopping}}^1$ to the deep level $\Delta_0^1$ are small due to strong suppression of mixing and hopping in this region of energy. The corrections from $vc^\dagger cZ$ are not so sensitive to the position of the $\Delta_0^1$-level and depends mainly in the density of $c$-charge or, since the contribution is local, just on number of $c$-electrons per $f$-cite. In order to visualize (see discussion in Ref. [37]) how this correction works, let us write it for a moment in the form $V_{nf}$. Then $E_{\Gamma_n} = \varepsilon_{0f} + \frac{1}{2}U n_f(n_f - 1) + V_{nc} n_f$ and we find that $\Delta_{\Gamma_{n+1}\Gamma_n} = \varepsilon_{0f} + U n_f + V n_c$, $\Delta_{\Gamma_n\Gamma_{n-1}} = \varepsilon_{0f} + U(n_f - 1) + V n_c$. Thus, the positions of both levels are essentially shifted by the Coulomb interaction with conduction electrons towards Fermi energy. But the effective Hubbard $U^*$ remains unchanged, $U^* = \Delta_{\Gamma_{n+1}\Gamma_n} - \Delta_{\Gamma_n\Gamma_{n-1}} = U$, until number of condition electrons $n_c$ remains unchanged. Therefore, main mechanism of a decrease of Hubbard $U$ is expected from the processes of dynamical screening or, in other words, from partial delocalization of wave functions of $f$-electrons. The calculations, based on the density-functional theory take into account these processes very efficiently (even slightly overestimate) giving, thus, much smaller values of $U^*$ than the bare value of $U$. Accurate evaluation of screening effects requires special analysis and we postpone it for a future work.

**VI. DISCUSSION AND CONCLUSIONS**

The theory presented here is intended mainly for those systems which contain a group of correlated electrons in the *strong-coupling* regime. The correlations have local, intra-atomic nature and therefore it is reasonable to construct a perturbation theory for the description of these electrons starting from the atomic limit. The technical difficulties in our approach come from the necessity to perform renormalization of fermion-fermion interactions in the *site* representation, which unavoidably leads to non-fermionic commutation relations of new on-site collective variables. This, in turn, makes it impossible to use standard Wick’s theorem for constructing a diagram technique. Besides, the site-centered single-electron wave functions, used for the formation of many-electron ones, are not orthogonal to functions of
other sites. In the case of weak Coulomb interaction one does not require the use of a non-orthogonal basis. However, for many band structure methods this may still be desirable, for technical reasons. In this work we have shown that Schwinger’s method\textsuperscript{32} of sources, which has become a standard method in solid state physics due to the work by Baym and Kadanoff\textsuperscript{30}, can be used for constructing a regular perturbation theory for systems with strongly correlated electrons and we have shown that this leads to important advantages. On one hand, this approach allows one to overcome the difficulties existing in the original formulation of the diagram technique from the atomic limit\textsuperscript{28,33} and to generalize the technique for \textit{d}- and \textit{f}-electron systems. On the other hand, the approach happens to be fruitful also in overcoming the difficulties which come from the necessity to use a non-orthogonal basis set. We hope also that, it gives a convenient tool to derive effective low-energy equations and to perform an analysis of corrections, arising beyond the standard Kohn-Sham equations. It is worth to note that since the theory is formulated in real space, it can be applied not only to the case of a regular lattice, but also to the case of impurity problems, or non-regular lattices. Of course, for the latter case an additional configurational averaging should be made. The perturbation theory developed here has a very close similarity to the ones for the boson and fermion systems. In particularly we have demonstrated this by the derivation of equations for the GFs: taking vertex in zero, first, and RPA approximations correspondingly, and we obtained the equations in the Hubbard-I, mean field, and RPA approximations.

Some important questions, however, remain to be solved. It is a well-known fact, that a direct calculations of Hubbard’s parameters for the Coulomb repulsion, for instance via the Slater integrals, give too large values. Within our theory the intra-atomic parameters enter the zero Hamiltonian, while the mixing and hopping become perturbations. The energies of intra atomic transitions of fermion type, which are determined by the bare value of Hubbard \textit{U} in the atomic limit and in the Hubbard-I approximation, are renormalized by mixing and hopping in our theory already in the next, mean-field approximation. These renormalized parameters still determine the positions of the centers of the correlated bands and the
structure of the equations for the renormalized energies of transitions is almost coinciding with the one within well-known non-crossing approximation. It is interesting to note that mathematically the mechanism is analogous to the Lamb shift in electrodynamics, but here it is provided by conduction electrons. The energy difference between the centers of these bands can be interpreted as renormalized Hubbard $U$ values. In a parallel work\(^{49}\) we have shown that, on one hand, the corrections, generated by the mixing interaction, can decrease or increase the value of effective Hubbard $U$ depending on the particular solution chosen. On other hand, this mechanism gives small corrections and cannot provide the expected reduction of Hubbard $U$.

In a series of works\(^{16, 15, 18}\) a separation of $f$-electrons into two subsystems, localized and delocalized, have been considered within the DFT approach on a phenomenological grounds. Application of the technique, developed in present work to this issue\(^{19, 20}\) gives solid grounds to this assumption and provides also a better insight. Particularly, it is shown that the role of the localized $f$-wave functions is played by the combination (25) of the transitions $[\Gamma_{n-1}, \Gamma_n]$ with an effective single-electron wave function,

$$
\Psi_f^{(\Gamma_{n-1}, \Gamma_n)}(r) \equiv \Psi_f^{lower}(r) \equiv \int d(r_1)d(r_2)\ldots d(r_{n-1})\Psi^*_{\Gamma_{n-1}}((r_1, r_2, \ldots, r_{n-1}, r_n)\Psi_{\Gamma_n}((r_1, r_2, \ldots, r_{n-1}, r),$$

(123)

corresponding to the lower-energy transition $\Delta_1$, while the delocalized $f$-wave functions correspond to combinations of wave functions

$$
\Psi_f^{(\Gamma_n, \Gamma_{n+1})}(r) \equiv \Psi_f^{upper}(r) \equiv \int d(r_1)d(r_2)\ldots d(r_n)\Psi^*_{\Gamma_n}((r_1, r_2, \ldots, r_n)\Psi_{\Gamma_{n+1}}((r_1, r_2, \ldots, r_{n+1})r),$$

(124)

The question how much the intra-atomic Coulomb $f-f$-interactions are renormalized by those corrections from the $(spd - f)$-interactions, which are not included in the standard LDA scheme is still open. One can expect that these interactions should provide a strong reduction of the effective $U^*$-s. This question is especially important for a calculation of the self-interaction correction (SIC), which plays a decisive role in the problem of volume-collapse transitions in rare earth metals\(^{55}\) and the theory of Mott insulators. We expect that
the expression for this correction, which arises in the equations of motion for the GFs when the self-energy is approximated by the difference between the static part of RPA-screened Coulomb interaction and the matrix element of the LDA potential, should be accurate. No problem with double counting and orthogonalization arises within such an approach.

The method suggested here is a special type of perturbation theory, which does not contain any approximations in its general formulation. The Hubbard-I approximation (HIA) and mean field approximation from atomic limit (AL-MFA) can be made with reasonably moderate efforts. It is relevant to emphasize here the similarities and differences between our AL-MFA from the popular method of dynamic mean field (DMF). The AL-MFA differs from the HIA by taking into account the renormalization of energies of intra-atomic transitions by mixing interaction and hopping. Therefore, besides self-consistent equations for many-electron population numbers, which arise in HIA, the system of equations for self-consistent centers of gravity of the Hubbard sub bands is present in the calculation in AL-MFA. A renormalization of this type is accounted for also in the DMF theory. However, it is not clear at the moment, to what extent they are different. Eq.(122) for the renormalized energies of intra atomic Fermi-type transitions in the AL-MFA is non-linear and sometimes contains more than one solution; the number of poles in the fermionic GF (or, number of Hubbard sub bands) is equal to the number of intra atomic fermionic transitions only near atomic limit. The DMF method is analogous to the coherent potential approximation and, therefore, can give some other poles. To be specific, the DMF gives a central peak in the density of states of fermionic excitations for the paramagnetic state of the s-band Hubbard model. The AL-MFA equation for renormalized energy of transition also may have second solution in vicinity of Fermi energy, what can provide the central peak in the density of electron states. However, in many cases the upper transition $\Delta_2$ being slightly above Fermi energy hybridizes with non-$f$ bands and gives birth to some tails under Fermi energy. These peaks are seen in electron spectroscopy and are close enough to Fermi energy in order to mask weak Kondo peak. The details of the mechanism of formation of these additional bands in the region of moderate coupling constants in terms of Hubbard-band
excitations remain to be elucidated. There is a difference between DMF and our approach in the treatment of spatial correlations. Namely, in applications of the DMF approach only a local, momentum-independent, self-energy has been considered, whereas in our theory first \((k, \omega)\)-dependent corrections in the expansion of the self-energy arises in the RPA (due to kinematic interactions).

At last, we note that it is easily seen from the close similarity between our construction of perturbation theory and the one by Baym-Kadanoff that the description of interacting delocalized and localized electrons in non-equilibrium states needs only slight generalization of our theory. Example of calculation of effects of non-orthogonality on the tunneling processes via a region with strongly interacting electrons is given in Ref. 48. An application of the technique to spin systems will be given elsewhere.

VII. ACKNOWLEDGMENTS

The authors are grateful to the Swedish Natural Science Council (NFR) and Göran Gustafsson Foundation for financial support. Part of this work has been performed in the Grup d’Electromagnetisme, Universitat Autònoma de Barcelona. I.S. thanks Prof. F.López-Aguilar and members of the group for hospitality and Ministerio de Educación y Ciencia of Spain for support (grant SAB95-0225) during his stay in Bellaterra. I.S. is also grateful to Prof. A.K. McMahan for valuable discussion of mechanisms of screening of Hubbard \(U\).

APPENDIX A: PARAMETERS OF THE HUBBARD-ANDERSON MODEL

Let us now discuss the parameters of the model. The energies \(E^0_\Gamma\) according to definition, are \(E^0_\Gamma = \langle \Gamma | H_{\text{ion}} | \Gamma \rangle\). For the case of Russel-Saunders coupling, i.e. for rare earths, corresponding expressions are given by Eqs. (7.18),(7.19) in Ref. 21. Main contributions to these energies come from pure Coulomb interaction,

\[
\delta E_{\Gamma,c} = \frac{1}{2} n(n - 1) F_{l=3}^{(0)} - \langle \Gamma | v^{LDA} | \Gamma \rangle.
\] (A1)
Typically, the bare $F^{(0)}$ are very large, $\sim 20\text{eV}$, what lead Hubbard to the conclusion that only the states with $n = n_0, n_0 \pm 1$ from the parabolic dependence of $E_\Gamma(n)$ can give contribution to the Hamiltonian. Here $n_0$ is dictated by the valence of the ion. As has been explained by McMahan, the interaction with non-$f$ electrons strongly decreases the $U_{\text{model}} = (\Delta_{\Gamma_{n+1},\Gamma_n} - (\Delta_{\Gamma_{n},\Gamma_{n-1}})$, where $\Delta_{\Gamma_p,\Gamma_q} \equiv (E_\Gamma - E_{\Gamma_m})$. It worth to emphasize the difference between our and Hubbard’s schemes. Hubbard and, also, Irkhin, diagonalized all on-site electrons, treating all of them in equal footing; this means that they have accepted the assumption that all on-site electrons are in strong-coupling regime. We assume that the conduction electrons (which are above tops of Coulomb barriers, can be described as a weakly-coupled subsystem.

Let us now discuss the mixing interaction. The matrix element $W$ in Eq.20 consists of three terms: $W_{\text{mix}} = W^{(1)} + W^{(2)} + W^{(3)}$. The term $W^{(1)} \sim Hc^+ f + H.c.$ describes the single-electron LDA-type of mixing, which is present in Eq.(8). This matrix element is:

$$W^{(1)}_{jL,j'\omega'} = \sum_{m'q} H_{jL,j'm'q}(f_{m'q})^d \equiv \sum_{m'q} H_{jL,j'm'q}\langle \Gamma_n | f_{m'q} | \Gamma_{n+1} \rangle$$

The other contribution to $H_{\text{mix}}$ arises from those terms of $(H - H_{\text{LDA}})$ which have the following operator structure; $c^+ X^a$ and $X^a c$. Obviously, the terms of the Coulomb interaction

$$\delta H_{\text{Coul}}^{\text{eff}} = C_{1234}^{\text{eff}} f_1^+ f_2^+ f_3 c_4 + C_{1234}^{\text{eff}} f_1^+ f_2^+ c_4 f_3 + C_{1234}^{\text{eff}} c_4^+ f_2^+ f_3 f_1 + C_{1234}^{\text{eff}} f_2^+ f_3^+ c_4^+ f_1^+ c_4^+ f_2^+ f_3 f_1,$$

which contain the $f-$operators related to the same site, should not be decoupled. We rewrite these products of $f$-operators in terms of $X$-operators,

$$(f_1^+ f_2^+ f_3) = \sum_{\tilde{a}} (f_1^+ f_2^+ f_3)^\tilde{a} X^{\tilde{a}}, \quad (f_3^+ f_2 f_1) = \sum_{\tilde{a}} (f_3^+ f_2 f_1)^\tilde{a} X^{\tilde{a}}.$$ 

In this place a possibility exists to consider a simplified models, omitting some terms of genius Coulomb interaction, but keeping corresponding terms in LDA. The Hartree part of the LDA potential contains these terms in the decoupled form. If we perform the decoupling of these terms in the Hartree-Fock fashion, there appears also exchange terms. However, the exchange interaction is treated within LSDA theory by the term $\sim (\alpha\rho^{1/3}(r))_{jL,jL'} a_{jL}^+ a_{jL'}$ in the potential. Therefore, it is reasonable to regroup the terms in order to represent every
term of the perturbation Hamiltonian in the form of a deviation of the non-approximated terms from the ones used in the LDA approach, as has been discussed in Sec.II. In order to avoid double counting we should not touch other terms of the Coulomb interaction if we do not consider its LDA-counterpart, if we do not take into account some of the Coulomb terms \((H - H_{LDA})_{Coul}\), corresponding terms enter all equations in the LDA form. Particularly, we treat in this way the terms of the form \(\sim Cc^+c^+cf\) and similar ones. Then we come to the following form for the remaining terms of the mixing matrix elements. For the density-density part we have,

\[
W_{jL,j'a'}^{(2)} = \sum_{\{m_{i}\},\sigma} C^{eff}_{jL,j'm_{i1}\sigma';j'm_{i2}\sigma';j'm_{i3}\sigma} \times [(f^\dagger_{m_{i1}\sigma'}f_{m_{i2}\sigma'})^{a'} - (f_{m_{i3}\sigma'})^{a'}(f^\dagger_{m_{i1}\sigma'}f_{m_{i2}\sigma'})^{LDA}] \\
\simeq \sum_{\{m_{i}\},\sigma} C^{eff}_{jL,j'm_{i1}\sigma';j'm_{i2}\sigma';j'm_{i3}\sigma} \times [(f^\dagger_{m_{i1}\sigma'}f_{m_{i2}\sigma'}f_{m_{i3}\sigma'})^{a'} - (f_{m_{i3}\sigma'})^{a'}\delta_{m_{i1},m_{i2}}n_{j'm_{i1}\sigma'}^{LDA}],
\]

(A4)

and for the exchange part,

\[
W_{jL,j'a'}^{(3)} = \sum_{\{m_{i}\},\sigma'} C^{eff}_{jL,j'm_{i1}\sigma';j'm_{i2}\sigma';j'm_{i3}\sigma} \delta_{m_{i2},m_{i3}} \delta_{\sigma,\sigma'} (f_{m_{i1}\sigma'})^{a'} n_{j'm_{i1}\sigma'}^{LDA} \\
- \sum_{m_{i},\sigma} (v_{xc}(r))_{jL,m_{i}\sigma} (f_{m_{i1}\sigma'})^{a'}. 
\]

(A5)

As seen the term \(\sim W_{jL,j'a'}^{(2)} \equiv 0\) for the empty orbitals. It is this matrix element that is responsible for the different mixing of conduction electrons with the intra atomic transitions \(f^{n-1} \rightarrow f^n\) and \(f^n \rightarrow f^{n+1}\). Obviously, this is a pure correlation effect: decoupling within the weak-coupling perturbation theory will make it vanish.

The prohibition to decouple the single-site products of \(f\)-operators leads to Coulomb renormalization of the LDA-hopping too:

\[
t^{\dagger}_{ab} = t_{1j}^{\dagger} + t_{2j}, 
\]

(A6)

\[
t^{\dagger}_{1j} = \sum_{\lambda\nu} [t^{\dagger}_{j}\lambda^{\dagger}\nu (f_{\lambda}^{\dagger}a)(f_{\nu}^{\dagger}b), \]

(A7)
Note the $t_2$-contribution from Coulomb interaction works similar to corresponding contributions to mixing: it makes hopping very different for, say, transitions $|\Gamma_{n-1}, \Gamma_n|$ and $|\Gamma_n, \Gamma_{n+1}|$.

**APPENDIX B: EXAMPLE: THREE-ELECTRON STATES AND COMMUTATION RELATIONS**

Let us consider a simple example of three electron states and corresponding commutation relations for the Hubbard operators, constructed on these states and belonging to the same site. A general three-electron state $|\Gamma\rangle$ can be written as follows:

$$|\Gamma\rangle = \sum_{\nu_1,\nu_2,\nu_3} C_{\nu_1,\nu_2,\nu_3}^\Gamma \theta_{\nu_1,\nu_2,\nu_3} f_{\nu_1}^\dagger f_{\nu_2}^\dagger f_{\nu_3}^\dagger |0\rangle,$$

Here $\theta$-functions are needed in order to establish a sign convention, i.e. in which order have to be taken the $f$-operators in the many-electron wave function; $\theta_{\nu_1,\nu_2} = 1$ if $\nu_1 > \nu_2$ and zero otherwise. Then, according to the definition of the $X$-operators, $X^{\Gamma_2\Gamma'} = |\Gamma\rangle \langle \Gamma'|$, the multiplication rule is:

$$X^{\Gamma_1} X^{\Gamma_2\Gamma'} = \langle \Gamma_1 | \Gamma_2 \rangle X^{\Gamma_2\Gamma'} = \nu_{\Gamma_1,\Gamma_2} X^{\Gamma_2\Gamma'}.$$  

From (B.1) we have

$$\langle \Gamma_1 | \Gamma_2 \rangle = \sum_{\nu,\mu} C_{\mu_1,\mu_2,\mu_3}^{\Gamma_1} C_{\nu_1,\nu_2,\nu_3}^{\Gamma_2} \theta_{\mu_1,\mu_2,\mu_3} \theta_{\nu_1,\nu_2,\nu_3} S_{\mu_3,\mu_2,\mu_1,\nu_1,\nu_2,\nu_3}.$$  

Then, from the anticommutation relation

$$\{ f_{\mu_1}, f_{\mu_2}^\dagger \} = \mathcal{O}_{\mu_1,\mu_2}^{-1},$$  

For the same site $n = m$ and we see that

$$\nu_{\mu_3,\mu_2,\mu_1,\nu_1,\nu_2,\nu_3} = \det \begin{vmatrix} \mathcal{O}_{\mu_1,\nu_1}^{-1} & \mathcal{O}_{\mu_1,\nu_2}^{-1} & \mathcal{O}_{\mu_1,\nu_3}^{-1} \\ \mathcal{O}_{\mu_2,\nu_1}^{-1} & \mathcal{O}_{\mu_2,\nu_2}^{-1} & \mathcal{O}_{\mu_2,\nu_3}^{-1} \\ \mathcal{O}_{\mu_3,\nu_1}^{-1} & \mathcal{O}_{\mu_3,\nu_2}^{-1} & \mathcal{O}_{\mu_3,\nu_3}^{-1} \end{vmatrix}.$$  

60
and, therefore, the commutation relation is given by

$$\{X^{\Gamma_1\Gamma}, X^{\Gamma_2\Gamma'}\} = \nu_{\Gamma_1\Gamma_2} X^{\Gamma_1\Gamma'} + \nu_{\Gamma_1\Gamma_2} X^{\Gamma_2\Gamma_1}. \quad (B6)$$

The equation of motion for the operator $X_i^{\Gamma_1\Gamma}$ contains the commutator

$$\sum_{n,\Gamma} \varepsilon_{\Gamma}[X_i^{\Gamma_1\Gamma_2}, h_n^{\Gamma}] = \sum_{n,\Gamma} [\nu_{i\Gamma_2,n\Gamma} \varepsilon_{\Gamma} X_{in}^{\Gamma_1\Gamma} - \nu_{n\Gamma,i\Gamma_1} \varepsilon_{\Gamma} X_{im}^{\Gamma_1\Gamma}], \quad (B7)$$

where

$$X_{im}^{\Gamma_1\Gamma} \equiv |i, \Gamma_1\rangle \langle n, \Gamma|. \quad (B8)$$

According to our assumption the direct overlap integral on wave functions of $f$-electrons belonging to different sites is negligible, therefore, main contribution comes from the terms with $i = n$, since $\nu_{i\Gamma_2,n\Gamma}$ involves determinant of the inverse of overlap matrix on $f-f$-matrix elements and each of them is proportional at least to second order of overlap between wave functions of band electrons and $f$-electrons. Without this approximation one has to solve problem of interacting via conduction electrons clusters. In this work we use the approximation

$$\sum_{n,\Gamma} \varepsilon_{\Gamma}[X_i^{\Gamma_1\Gamma_2}, h_n^{\Gamma}] \approx \sum_{\Gamma} [\nu_{i\Gamma_2,i\Gamma_1} \varepsilon_{\Gamma} X_i^{\Gamma_1\Gamma} - \nu_{i\Gamma_1,i\Gamma_1} \varepsilon_{\Gamma} X_i^{\Gamma_1\Gamma}] \approx \Delta_{\Gamma_2\Gamma_1} X_i^{\Gamma_1\Gamma_2} \quad (B9)$$

with

$$\Delta_{\Gamma_2\Gamma_1} \equiv \nu_{i\Gamma_2,i\Gamma_2} \varepsilon_{\Gamma_2} - \nu_{i\Gamma_1,i\Gamma_1} \varepsilon_{\Gamma_1}. \quad (B10)$$

**APPENDIX C: EQUATIONS OF MOTION FOR OPERATORS**

1. Equations of motion for quasi-fermion operators

In order to construct equations for the Green’s functions we need the equations of motion $i\partial_t \hat{F} = [\hat{F}, \hat{H} - \mu \hat{N}]$ for (quasi)fermions. As seen from Eq.(28), the particle number operator has the same operator structure as the Hamiltonian (26-27). Therefore, in order to obtain $\hat{H} = \hat{H} - \mu \hat{N}$, we should make the simply the following shifts:
\[ E_1^0 \rightarrow \tilde{E}_1^0 = E_1^0 - \mu \sum_M (n_{MM}) \Gamma, \]  
(C1)

\[ H_{jL,j'L'} \rightarrow \tilde{H}_{jL,j'L'} = H_{jL,j'L'} - \mu O_{jL,j'L'}, \]  
(C2)

\[ t_{jj'}^{aa'} \rightarrow \tilde{t}_{jj'}^{aa'} = t_{jj'}^{aa'} - \mu \sum_{M_1M_2} (1 - \delta_{jj'}) (f_{M_1}^j)^a O_{jM_1,j'M_2} (f_{M_2}^{j'})^{a'}, \]  
(C3)

and

\[ W_{jL,j'a} \rightarrow \tilde{W}_{jL,j'a} = W_{jL,j'a} - \mu \sum_M O_{jL,j'M} (f_M)^a, \]  
(C4)

in the Hamiltonian \( H \). Below we assume that such a shift has been made, and will accordingly drop the tilde. Then the equations of motion for the \( c \)- and \( X \)-operators can be written as:

\[ i \partial_t c_{jL} = \sum_{j_2L_2} (O^{-1} H)_{jL,j_2L_2} c_{j_2L_2} + (M_c)_{jL}, \]  
(C5)

\[ i \partial_t X^a_j = \Delta a X^a_j + (M_X)^a_j \]  
(C6)

where for \( a = [\Gamma_{n-1}, \Gamma_n] \) the energy of the transition \( \Delta a = E_{\Gamma_n} \nu_{\Gamma_n} - E_{\Gamma_{n-1}} \nu_{\Gamma_{n-1}} \). The coefficient \( \nu = 1 \) when the \( f \)-orbitals are orthogonal to other and \( \nu < 1 \) when they are not. The operator \( M \) describes deviations from the solution at zero mixing interaction in the particular potential chosen (say, LDA). The \( M \)-operator for the \( c \)-subsystem consists of linear and non-linear parts,

\[ (M_c)_{jL} = (M_{c}^{lin})_{jL} + [(M_{c}^\uparrow)_{jL} - (M_{c}^\downarrow)_{jL}], \]  
(C7)

where the linear one is given by

\[ (M_{c}^{lin})_{jL} = \sum_{j_2L_2} w_{jL,j_2L_2} X^a_{j_2}, \]  
(C8)

and

\[ w_{jL,j_2a} \equiv (O^{-1} W)_{jL,j_2a} \]  
(C9)
The non-linear terms are given by the operators \((M^\uparrow_c)_{jL}, (M^\downarrow_c)_{jL}\) which can be written in the form

\[
(M^\uparrow_c)_{jL} = \sum (O^{-1})_{jLj_1M} (f_M)^c \hat{P}_{j_1}^{ab} [d_{j_1j_2}^a X_{j_2}^b + W_{j_1j_2}^* c_{j_1}^a c_{j_2}^c] \quad (C10)
\]

and

\[
(M^\downarrow_c)_{jL} = \sum (O^{-1})_{jLj_2M} (f_M)^c [d_{j_1j_2}^a X_{j_1}^b + W_{j_1j_2}^* c_{j_1}^a c_{j_2}^c] \hat{P}_{j_2}^{ca} . \quad (C11)
\]

Here \(\hat{P}_{a,b} \equiv \{X^a, X^b\} \equiv \epsilon a, \bar{b} Z^\xi, \quad \hat{P}_{a,b} \equiv \{X^a, X^b\} \equiv \epsilon a, \bar{b} Z^\eta\). The expression for the \(M\)-operator of the \(f\)-subsystem can also be written in the form

\[
(M_X)_j = [(M^\uparrow_X)_j - (M^\downarrow_X)_j] \quad (C12)
\]

with

\[
(M^\uparrow_X)_j = \sum t'^{bc}_{jj_2} \hat{P}_{j_2}^{bc} \quad (C13)
\]

\[
(M^\downarrow_X)_j = \sum t'^{bc}_{jj_2} \hat{P}_{j_2}^{bc} \quad (C14)
\]

Here the matrix elements are given by the following combinations

\[
w_{j_1b,j_2L_2}^\dagger = W_{j_1b,j_2L_2}^* + \sum_M (f_{jM}^\uparrow)^b (O^{-1*}H)_{jM,j_2L_2}, \quad (C15)
\]

\[
t^{bc}_{jj_2} = t^{bc}_{jj_2} + \sum_M (f_{jM}^\uparrow)^b (O^{-1*}W)_{jM,j_2c} \quad (C16)
\]

Some features of the correlated electron system can be seen already from these equations.

**First**, we see that instead of equations for \(f\)-operators, as in case of non-correlated electrons, we have to write equations for their complicate combinations \(X^a\). This leads to an unpleasant consequence: the number of variables and, correspondently, equations, increases drastically; every \(f\)-operator is split into many Hubbard sub-amplitudes. The number of transitions involved depends on the valence of the \(f\)-ion.

**Second**, we find that due to non-orthogonality the \(f\)-level also contributes to the mixing interaction: the term in Eq.45 describing linear mixing would disappear for the orthogonal basis.
Third, the non-orthogonality transfers non-linearity into the conduction electron subsystem. This correctly reflects the underlying physics; the $c$-electron spends part of its life as an $f$-electron, therefore, the mixing and hopping which it experiences should be correlated to the same extent. It is this reasoning which forced us to perform operations in this particular order. First, we take into account correlations, and then perform orthogonalization. The other motivation is of a technical nature; this construction allows us to avoid consideration of a combinatorics of tails for vertexes with one $c$-tail and many $f$-tails. On the other hand if we now decide to write the equations in terms of $f$-electrons (i.e., fermion $f$-operators), some features of the many-tail vertexes are clarified by these equations. Particularly, the many-electron GFs, which are not allowed to be decoupled, can be obtained simply by transformation of all Hubbard’s operators back to the $f$-operator form.

Fourth, the equation for the $X$-operator does not contain linear mixing.

Fifth. The right-hand side of the equation has some similarity to the Boltzmann equation; both contributions, from mixing and from hopping, consist of two terms, "incoming" and "outgoing"; we denote them by the superscripts $\uparrow$ and $\downarrow$, correspondingly, in order to emphasize that the first describe intra-atomic transitions "up", from the states with $n$ electrons to the states with $n+1$ electrons; the $\downarrow$-terms describe the inverse processes. As we have seen above (see, e.g., discussion after Eq.110) later, the contributions from the latter terms always contain a small parameter.

2. Equations of motion for quasi-boson operators

Let us introduce the vector-operator $\eta$, which will describe all fermion or fermion-like transitions in our system. For example, for the system with $n$ conduction bands and $m$ intra-atomic fermi-like transitions it is given by:

$$\eta_{j \lambda}^\dagger = (c_{jL_1}^\dagger, \ldots, c_{jL_n}^\dagger, X_{j1}^{b_1}, \ldots, X_{jn}^{b_m}, c_{jL_1}, \ldots, c_{jL_n}, X_{j1}^{h_1}, \ldots, X_{jn}^{h_m}). \quad (C17)$$

As is seen from this notation, for $\eta = c$ or $c^\dagger$ the index $\lambda$ takes a value $L$ while for $\eta = X$
or $X^\dagger$, and $\lambda$ can either be $b$ or $b^\dagger$. The Hamiltonian without external fields generates the following equation of motion for the operators $Z^\xi$:

$$i\partial_t Z^\xi_j = \sum_\Gamma \delta_{\xi,\Gamma} \Delta^\xi_j + V^\xi n_{1L_j} b c_{n_{1L_j}} X^b + V^\xi j b n_{1L_j} X^b c_{n_{2L_j}} + V^\xi n_{1\bar{a}_1,n_{2a_2}} [\delta_{n_{1j},\bar{a}_1} b + \delta_{n_{2j},a_2} b] X^\bar{a}_1 X^a_2;$$

$$\equiv \sum_\Gamma \Delta^\xi_j + V^\xi n_{1\lambda_1,n_{2\lambda_2}} \eta^\dagger_{n_{1\lambda_1}} \eta_{n_{2\lambda_2}}. \quad (C18)$$

Let us remind the reader that for the diagonal operators (i.e., for the transition $\xi = [\Gamma, \Gamma]$) the first term in the right-hand side of Eqn.C18 vanishes, since for this transition $\Delta_{\xi=[\Gamma,\Gamma]} = \nu_{TT} E_T - \nu_{TT} E_T = 0$. Furthermore, we have defined the constants of the interaction in such a way that $V^\xi n_{1\lambda_1,n_{2\lambda_2}} = 0$ when $(n_{1\lambda_1}) = (n_{1L_1})$ and $(n_{2\lambda_2}) = (n_{2L_2})$ simultaneously, i.e. when both indices relate to $c$-electrons. In all other cases they denote the following combinations of the matrix elements:

$$V^\xi j b n_{2L_2} \equiv -O^{-1}_{jM,n_{1L_1}} (f^\dagger_M)^c \varepsilon_b \bar{c}_b h_{n_{1L_1},n_{2L_2}} + W^*_{j\bar{a}_1,n_{2L_2}} \varepsilon_a^\dagger; \quad (C19)$$

$$V^\xi n_{1L_1,jb} \equiv -O^{-1}_{n_{2L_2},jM} (f^\dagger_M)^c \varepsilon_b \bar{c}_b h_{n_{1L_1},n_{2L_2}} + W^*_{n_{1L_1},ja_2} \varepsilon_a^\dagger; \quad (C20)$$

$$V^\xi n_{1\bar{a}_1,jb} \equiv -O^{-1}_{n_{2L_2},jM} (f^\dagger_M)^c \varepsilon_b \bar{c}_b W^*_{n_{1\bar{a}_1},n_{2L_2}}; \quad (C21)$$

$$V^\xi n_{1\bar{a}_1,jb} \equiv -W_{jL_1,n_{2a_2}} O^{-1}_{jM,n_{1L_1}} (f^\dagger_M)^c \varepsilon_b^\dagger. \quad (C22)$$

**APPENDIX D: AUXILIARY FIELDS $A_{j\lambda,j'\lambda'}(T)$**

The auxiliary fields $A_{j\lambda,j'\lambda'}(t)$ have the following non-zero elements:

For $\eta_\lambda = c$ we have

$$A^{(cX)}_{jL,j'a}(t) = \sum_{j'Mb,\xi=\eta,\lambda,\Gamma} \varepsilon_b^\dagger_{a} U_{j'M}(t)(f^\dagger_M)^b (O^{-1})_{jL,j'M} \quad (D1)$$

and

$$A^{(cX^\dagger)}_{jL,j'a}(t) = \sum_{j'Mb,\eta} \varepsilon_b^\dagger_{a} U_{j'M}(t)(f^\dagger_M)^b (O^{-1})_{jL,j'M}. \quad (D2)$$

For $\eta_\lambda = X$ we have
\[ A_{j_{a,j',b}}^{(XX)}(t) = \sum_{\xi=\eta,A,\Gamma} \varepsilon^\xi_{b} U_{j_{\xi}}(t) \delta_{j_{j',a}} A_{j_{b}} \]  

(D3)

and

\[ A_{j_{a,j',b}}^{(XX^\dagger)}(t) = \sum_{\bar{\eta}} \varepsilon_{b}^{\bar{\eta}} U_{j_{\bar{\eta}}} U_{j_{\bar{\eta}}}^*(t) \delta_{j_{j',a}} A_{j_{b}}. \]  

(D4)

For \( \eta_{\lambda} = c^\dagger \) we have

\[ A_{j_{L,j',b}}^{(c^\dagger X^\dagger)}(t) = - \sum_{\xi=A,\bar{\eta},\Gamma M_a} \varepsilon_{b}^{\bar{\xi}} U_{j_{\xi}}(t) (f_M)^{\bar{a}} (O^{-1})_{j'M,jL} \]  

(D5)

and

\[ A_{j_{L,j',b}}^{(c^\dagger X)}(t) = - \sum_{\bar{\eta} M_a} \varepsilon_{b}^{\bar{\xi}} U_{j_{\bar{\eta}}} U_{j_{\bar{\eta}}}^*(t) (f_M)^{\bar{a}} (O^{-1})_{j'M,jL}. \]  

(D6)

For \( \eta_{\lambda} = X^\dagger \) we have

\[ A_{j_{a,j',b}}^{(X^\dagger X^\dagger)}(t) = - \delta_{j_{j'}} \sum_{\xi=\bar{\eta},A,\Gamma} \varepsilon_{b}^{\bar{\xi}} U_{j_{\xi}}(t) \equiv \delta_{j_{j'}} A_{j_{b}} \]  

(D7)

and

\[ A_{j_{a,j',b}}^{(X^\dagger X)}(t) = - \delta_{j_{j'}} \sum_{\eta} \varepsilon_{b}^{\eta} U_{j_{\eta}}(t) \equiv \delta_{j_{j'}} A_{j_{b}}. \]  

(D8)
REFERENCES

1 P. Hohenberg and W. Kohn Phys.Rev. 136 864 (1964); W. Kohn and L.J. Sham Phys.Rev. 140A 1133 (1965).

2 B.Brandow, Adv. Phys. 26, 651 (1977).

3 I.S. Sandalov and V.I. Filatiev, Physica B162, 139;162 (1990).

4 M.B.J. Meinders, H. Eskes, G.A. Sawatsky, Phys. Rev. B 48, 3916 (1993-II).

5 W.M. Temmerman and Z. Szotek, Phys. Rev. B 47 4029 (1993).

6 J.P. Perdew, A. Zunger, Sol. St. Comm. 34, 933 (1980); Phys. Rev. B 23, 5048 (1981).

7 A.M.Boring, R.C.Albers, O.Eriksson, and D.D.Koelling, Phys. Rev. Lett. 68, 2652 (1992).

8 V.I. Anisimov, J. Zaanen and O.K. Andersen, Phys. Rev. B44, 943 (1991).

9 I. S. Sandalov, O. Hjortstam, B. Johansson, and O. Eriksson, Phys. Rev. B 51, 13 987 (1995-II).

10 E.G. Maksimov, I.I. Mazin, S.Yu. Savrasov and Yu.A. Uspenski, J. Phys. C: Condens. Matter 1 2493 (1989).

11 L.J. Sham, Phys. Rev. B32 3876 (1985), W. Hanke, N. Meskini, and H. Weiler, Electronic Structure, Dynamics, and Quantum Structural Properties of Condensed Matter, ed. J.T. Devreese and P. Van Camp, Plenum Press, NY and London.

12 J. Hubbard, Proc. Roy. Soc. 276A, 238 (1963).

13 J. Hubbard, Proc. Roy. Soc. 277A, 237 (1964).

14 U. Lundin, I. Sandalov, O. Eriksson, B. Johansson, Physica B259-261, 231 (1990).

15 U.P. Strange, A. Svane, W.M. Temmerman, Z. Szotek, H. Winter, Nature bf 339Æ 756 (1999).
16 C. Lehner, M. Richter, H. Eschrig, Phys. Rev. B\textbf{58}, 6807 (1998).

17 N. Grewe, Z.Physik B (Cond. Mat.) \textbf{67}, 323 (1987); N. Grewe, T. Pruschke, H. Keiter, Z.Physik B (Cond. Mat.) \textbf{71} 75 (1988).

18 O. Eriksson, J.D. Becker, A.V. Balatsky, J.M. Wills, Journ. of Alloys and Compounds, \textbf{287}, 1 (1999).

19 I. Sandalov, B. Johansson, O. Eriksson, Physica \textbf{B259-260} 229 (1999).

20 U. Lundin, I. Sandalov, B. Johansson, and O. Eriksson (to be published).

21 V. Yu. Irkhin and Yu. P. Irkhin, Phys. Stat. Sol. (b) \textbf{183}, 9 (1994).

22 M.S.S. Brooks, O. Eriksson, J.M. Wills, and B. Johansson, Phys. Rev. Lett., \textbf{79} 2546 (1997). L. Severin and T. Gashe, M.S.S. Brooks, B. Johansson, Phys. Rev. B\textbf{48}, 13 547 (1993).

23 N.M. Rosengaard and B. Johansson, Phys. Rev. B \textbf{55} 14 975 (1997-II).

24 L.D. Faddeev, Sov. Phys. JETP \textbf{12}, 1014 (1961) (transl. from Russian: ZhETF 1459 (1960)).

25 Y. Kuramoto, Z. Phys. B - Cond. Matter \textbf{53}, 37 (1983).

26 N. Grewe, Z. Phys. B - Cond. Matter, (1983).

27 B. Westwański and A. Pawlikowsky, Phys. Lett. A \textbf{43}, 1458 (1973).

28 R.O. Zaitsev, Zh. Eksp. Teor. Fiz. \textbf{70}, 1100 (1976),- in Russian (Engl. transl.: Sov. Phys. JETP, \textbf{43}, 574 (1976)).

29 M. Yu. Nikolaev, N. V. Ryzhanova, A.V. Vedyaev, and S. M. Zubritskii, Phys. Stat. Solidi (b) \textbf{128}, 513 (1985).

30 G. Baym, L.P. Kadanoff, Phys. Rev. B 124, 287 (1961).
31 A.E. Ruckenstein, S. Schmitt-Rink, Phys. Rev. B 38, 7188 (1988).

32 J. Schwinger, J. Math. Phys. (N.Y.) 2 407 (1961).

33 Yu.A. Izyumov, B.M. Letfulov, and E.V. Shiipizyn, M. Bartkowiak and K.A. Chao, Phys. Rev. B 46, 15 697 (1992-II).

34 S. V. Beiden, N. E. Zein and G.D. Samoiljuk, Phys. Lett. A 177, 167 (1993).

35 N. E. Zein, Phys. Rev. B 52, 11 813 (1995-II), 177 167 (1993).

36 B.R. Judd, Operator Technique in Atomic Spectroscopy, McGraw-Hill Publ.Co., New York 1963.

37 A.K. McMahan, R.M. Martin, S. Satpathy, Phys. Rev. B 38, 6650, (1988); A .K. McMahan, J.F. Annet, and R.M. Martin, Phys. Rev. B 42, 6268 (1990).

38 H. Eschrig, Optimized LCAO Method and the Electronic Structure of Extended Systems, Akademie-Verlag, Berlin, 1988.

39 O.K. Andersen, Phys. Rev. B12, 3060 (1975).

40 H.I. Skriver, The LMTO Method; Springer: Berlin, 1984.

41 J.M. Wills and B. R. Cooper, Phys. Rev. B36, 3809 (1987).

42 O. Gunnarsson, O. K. Andersen, O. Jepsen, and J. Zaanen, Phys. Rev. B39 1708 (1989).

43 V.Yu. Yushankhai, N.M. Plakida, P. Kalinay, Physica C174, 401 (1991).

44 Yu. A. Izyumov, B.M. Letfulov, Journ. of Phys.: Cond. Matt. 3 5373 (1991).

45 I.S. Sandalov, B. Johansson, Physica B 206 & 207 712 (1995).

46 R.M. White, P. Fulde, Phys. Rev. Lett. 47 1540 (1981).

47 P. Fulde, J. Jensen, Phys. Rev. B 27 4085 (1983).

48 E.V. Kuz’min, I.S. Sandalov, Sov. Phys.-Zh.Exp.Teor.Fiz. 68 1388 (1975).
49 U. Lundin, I.S. Sandalov, O. Eriksson, B. Johansson, Physica B259-261, 231 (1999).

50 A. K. McMahan, C. Huscroft, R.T. Scalettar, and E.L.Pollok, Volume-collapse transition in the rare earth metals, Preprint.

51 A. Georges, G. Kotliar, W. Krauth, M.J. Rosenberg, Rev. Mod. Phys. 68, 13 (1996).

52 See discussion of this question in the book by P. Fulde, Electron Correlations in Molecules and Solids, third enlarged edition, Springer, p.290; the Eq.(12.2.18-19) has the same form as our Eq.(98,99).

53 Y.Baer and W.-D. Schneider, in Handbook on the Phys. and Chem. of the Rare Earths, vol.10, p.1 (North-Holland, Amsterdam 1987).

54 We believe that it is erroneous to name ”Kondo resonanse” for this peak ”Kondo resonance” since it may exist even in spinless system. The relevant discussion in connection with quantum dots is given in: J. Fransson and I. Sandalov, Proceedings of ICM 2000, Brasil, to be publ.
FIGURES

FIG. 1. Corrections to the self-energy in the approximation Hubbard-I (Eq. 78). The dashed wiggle line denotes the part of mixing $\theta^\Gamma$, the triangle with inscribed $\alpha$ denotes the $\alpha$-matrix, given by Eq.64, the mixing interaction is denoted by the wiggle line (see Eq.84). The expectation value $\langle Z_{3b} \rangle$ is denoted by circle-cross on the top of the $\alpha$-triangle. Summation over bosonic index $I_b$ is implied in this top what transforms the product $\alpha_{12,3b} \langle Z \rangle$ into $P_{12}$.

FIG. 2. Simplification of the graphical notations in the case of equations for fermions. In the vertex containing $\alpha$-matrix the line of mixing interaction goes out of the vertex, while in the one containing $\beta$-matrix it enters the vertex; $\beta$-matrix appears always together with the $\tau$-matrix (see Eqs.64, 72 and 88), which inverts direction of the line of mixing. This vertex describes the process involving two-electron ($\Gamma_{n-2} \rightarrow \Gamma_n$)-transition.

FIG. 3. $R^l$-rule of taking functional derivatives of the pseudolocator line; changing $\alpha$ by $\beta$ gives $R^r$-rule (see Eqs.85 and 86,87).

FIG. 4. Mean field corrections to the self-energy of pseudolocator. Note that both vertexes have three tails of pseudolocators and one of interaction; left vertex has the outgoing interaction tail, while right one has incoming interaction tail. The point from which the dashed line of $\eta$-pseudolocator and the wavy line of the $\eta-\eta$-interaction $V_{12}$ go out denotes the $\tau$-matrix.

FIG. 5. The second-order corrections to the vertexes from kinematic interactions.

FIG. 6. Corrections to the self-energy of the $\eta$-pseudolocator generated by the second-order corrections to vertex.