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Poisson equation and a self-consistent periodical Anderson model

U. Lundin, I. Sandalov, and O. Eriksson
Condensed Matter Theory Group, Uppsala University, Box 530, SE-751 21 Uppsala, Sweden

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We show that the formally exact expression for the free energy (with a nonrelativistic Hamiltonian) for the correlated metal generates the Poisson equation within the saddle-point approximation for the electric potential, where the charge density automatically includes correlations. In this approximation the problem is reduced to the self-consistent periodical Anderson model. The parameter of the mixing interaction in this formulation have to be found self-consistently together with the correlated charge density. The factors, calculated by Irkhin, for the mixing interaction, which reflect the structure of the many-electron states of the f ion involved, arise automatically in this formulation and are quite sensitive to the specific element we are interested in. We also discuss the definitions of the mixing interaction for the mapping from *ab initio* to model calculations.

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I. INTRODUCTION

The local density approximation (LDA) to the density functional theory (DFT) is working surprisingly well in many cases for which it is expected not to work at all. One of its most important features is that the self-consistent procedure provides a quite accurate distribution of the charge density, calculated from the Kohn-Sham equation,[1] which is more accurate than the Poisson equation. It is also important to understand why the form of the potential that has been derived from the theory of a *homogeneous* electron gas with the charge density that includes contributions from the localized electrons (the extreme case of nonhomogeneity) works so well. Below we will show that, at least, the Poisson equation can be formulated also in the case of strongly correlated systems, where some part of the electrons are either fully or partly localized. On one hand, physically it is clear that the role played by the localized (core) electrons in the formation of the potential is the screening of the nuclear potential experienced by the conduction electrons (which contribute to the cohesive energy). The localized electrons do not contribute to the cohesive energy, and therefore the error, coming from an insufficient description of the core electrons, is not so essential for the properties derived from a calculation of the total energy at zero temperature. On the other hand, the experience accumulated using the DFT shows that it fails to describe the properties that require information about (quasi)localized electrons, as in photoelectron spectroscopy experiments, or exchange interactions among localized electrons in magnetic insulators, semiconductors, etc. In these cases, methods either completely based on field theory or those combining field theory and DFT are desirable. The models often used are the Anderson impurity and periodical models and here we will discuss mainly the periodical model. There are two ways for providing methods that combine DFT and field theory. The first way is the following. The field operators can be constructed using the functions generated within a LDA-DFT calculation, and a correction, constructed from the difference $\mathcal{H}^{\text{int}}=\mathcal{H}^{\text{full}}-\mathcal{H}^{\text{LDA}}$, can be used to correct the electronic structure generated by the initial LDA calculation.[2] The motivation for using the LDA-DFT basis here is that one can expect compensation by the LDA potential from a part of the self-energy for the conduction electrons, which corresponds to a static random phase approximation.[3] This way, however, involves complex calculations of the matrix elements of the Coulomb interaction and frequency-dependent magnitudes, such as the self-energy, such that in practice these calculations are quite hard to perform.[4,5] The other way, used much more often, is through some mapping to the Anderson or Hubbard models. Then, two difficulties arise. *First*, the question about double counting of some of the interactions, and also how to calculate the parameters of the model that is chosen for treating correlations. *Second*, the model calculations often involve a redistribution of spectral weights between low- and high-energy regions and a redistribution of the charge density caused by it. The latter is never taken into account in the model calculations. It is especially important since any redistribution of charge involves a large Coulomb energy. This is especially important when the Anderson model is used for discussing magnetic properties. These properties are determined by the effective exchange integral $\sim V^2/U$ (where V is the mixing and U is the Hubbard on-site repulsion) and therefore involve *small* energies. Calculations of this small energy difference, having neglected a possibly greater Coulomb energy, can easily lead to a misinterpretation of the experimental data. It is also important that the mixing interaction is representation dependent and, therefore, for the description of a real system within a model it is important to define clearly what is mixing interaction for that special case. This shows the need for a formulation that allows for a self-consistent calculation of the parameters of the model together with the charge density. Such an opportunity arises in a natural way if one starts with the full Hamiltonian and treats the single-ion Coulomb interactions in some approximation that takes into account the strong local electron correlations. Such a scheme has been suggested earlier;[6] however, the strong electron correlations (SEC) have been treated within the slave-boson technique, which at present seems to be unsatisfactory for reasons that we will not discuss here.[7] Here we will discuss the parameters of the Anderson model within the same scheme, using the definitions of the operators in a nonorthogonal basis set that is different from Ref. 6, but coincides with those used in Ref. 2 and 8. We have discussed a way to calculate the single-site Coulomb repulsion parameter, Hubbard *U*, earlier.[2,8,9] Here we pay attention mainly to the mixing interaction. The organization of the paper is as follows. In Sec. II we rewrite the Hamiltonian in a nonorthogonal basis set and construct the many-electron operators. Using a saddle-point approximation we get the Poisson equation for the SEC system. In Sec. III we show how the periodical Hubbard-Anderson model appears using the results of Sec. II. In Sec. IV we discuss the mixing parameter entering the model, and in Sec. V we conclude with a discussion.

II. THE POISSON EQUATION IN THE SYSTEM WITH SEC

Here we reformulate the derivation given in Ref. 6, but within a nonorthogonal basis set, and we avoid the slave-boson technique. Let us consider an ion that has a number *n* of *f* electrons in the ground state. Then, only the transitions $\Gamma_n \rightarrow \Gamma_{n\pm 1}$ will be allowed in the spectrum of excitations while all other transitions such as $\Gamma_n \rightarrow \Gamma_{n\pm 2}, \Gamma_{n\pm 3}$, involving a larger number of electrons, will be strongly suppressed by the large energy separation between these states. If the energy of the atomiclike transition $\Delta_2 \equiv E_{\Gamma}^{(n+1)} - E_{\Gamma'}^{(n)}$ between an $(n+1)$- and *n*-electron state, Γ and Γ', of the *f* ion is much higher than the Fermi energy, ε_F, the number of *f* electrons in the ion will be fixed. Indeed, in this limit this upper "single-electron" level is empty while the lower one, even if it forms a band, will be fully filled. In the rare earth elements the populated part of the *f*-electron spectral density corresponding to the transitions $\Delta_1 \equiv E_{(n)} - E_{(n-1)}$ is much lower than ε_F (except for Ce, and perhaps Sm). It can be also much lower than the bottom of the conduction-electron bands. When an orbital has such a low energy, the mixing interaction, as well as overlap between these corelike levels and conduction electrons are negligible.[10] This physical picture corresponds to the type of *ab initio* calculation where the *f* electrons are kept in the core. One can use the many-electron functions for the description of the ground state of an ion from DFT-LDA-based calculations too. All electrons in this case experience the same potential. As has been shown in Ref. 8, this picture is valid when the energy of the upper transition, $\Delta_2 = E_{(n+1)} - E_n$, is much greater than the Fermi energy. However, the photoelectron spectroscopy experiments show that even in rare earth elements, for which this picture seems to be most appropriate, the level Δ_2 is sometimes only slightly above ε_F.[11] Therefore, due to the mixing interaction and, possibly, hopping, a band with mixed *f*-electron and conduction-electron states[12] can be formed. As discussed in detail in Ref. 8, this leads to shifts of spectral weights from integer values and a violation of the single-electron picture. These spectral weights, therefore, must enter the expression for the charge density in the Poisson equation. Besides, they control the strength of the mixing and hopping. Let us derive the Poisson equation, which contains information about these spectral weights and is valid not only for zero temperature. Here, we will neither consider the formation of phonons and scattering processes that involve them, nor plasmons.

A. The Hamiltonian in a nonorthogonal basis set

An orthogonalization procedure of the wave functions belonging to different ions leads to a coupling of the states. This makes it difficult to separate the strongest single-site interactions. Therefore, the local strong interactions between *f* electrons can most easily be taken into account in the *non-orthogonal* site representation. For this reason we will, to some extent, use the technique developed previously[2] (below referred to as I). The delocalized electrons are treated within the weak-coupling perturbation theory (WCPT), while the localized (or semi-localized) within the strong-coupling theory (SCPT), see paper I. In order to introduce, for the *f* operators (and other core electrons), the many-electron representation we rewrite the field operator, $\hat{\psi}_\sigma(\mathbf{r})$, in the jL representation

$$\hat{\psi}_\sigma(\mathbf{r}) = \int d\mathbf{q}\, e^{-i\mathbf{q}\cdot\mathbf{r}} \phi_{jL}(\mathbf{r}) a_{jL}, \tag{1}$$

$$a_{jL} = [(1-\delta_{L,\mu})c_{jL} + \delta_{L,\mu} f_{j\mu}]. \tag{2}$$

Here, $j \equiv R_j$ is the site, $L \equiv (l, m_l, s = 1/2, \sigma)$, l is the orbital moment, m_l is its projection to the z axis, s is electron spin, and σ, its projection to the same axis μ, indicates localized electrons. In Eq. (2) we have separated all electrons into two classes: core electrons, $f_{j\mu}$, which either remain fully localized in solids or only partly delocalized, and delocalized electrons, c_{jL}, which will be described in **k** space in regular crystals. Since the essential part of the work to be done concerns the localized electrons, it is reasonable to formulate the approach in the site representation first. The basis functions $\phi_{jL}(\mathbf{r})$ are in general not orthogonal to each other,

$$\int d\mathbf{r}\, \phi^*_{jL}(\mathbf{r}) \phi_{j'L'}(\mathbf{r}) = \mathcal{O}_{jL,j'L'}. \tag{3}$$

Therefore, from $\{\psi_\sigma(\mathbf{r}), \psi^\dagger_{\sigma'}(\mathbf{r}')\} = \delta(\mathbf{r}-\mathbf{r}')\,\delta_{\sigma\sigma'}$, we see that

$$\{a_{jL}, a^\dagger_{j'L'}\} = \mathcal{O}^{-1}_{jL,j'L'}, \tag{4}$$

where $\mathcal{O}^{-1}_{jL,j'L'}$ is the $(jL, j'L')$ matrix element of the inverse of the overlap matrix $\mathbf{O}$.

The full Hamiltonian is

$$\begin{aligned}\mathcal{H} = \int d\mathbf{r}\, \psi^\dagger_\sigma(\mathbf{r}) \left[\frac{p^2}{2m} - \sum_j \frac{Z_j e^2}{|\mathbf{r}-\mathbf{R}_j|} - C_\infty \right] \psi_\sigma(\mathbf{r}) + \mathcal{H}_{nn} \\ + \frac{1}{2} \int d\mathbf{r}\, d\mathbf{r}'\, \psi^\dagger_\sigma(\mathbf{r}) \psi_\sigma(\mathbf{r}) v(\mathbf{r}-\mathbf{r}') \psi^\dagger_{\sigma'}(\mathbf{r}') \psi_{\sigma'}(\mathbf{r}'),\end{aligned} \tag{5}$$

$$\mathcal{H}_{nn} = \sum_j \frac{Z_i Z_j e^2}{|\mathbf{R}_i - \mathbf{R}_j|}, \tag{6}$$

where C_∞ is the infinite constant $\int d\mathbf{r} d\mathbf{r}'\, \delta(\mathbf{r}-\mathbf{r}') v(\mathbf{r}-\mathbf{r}') \Sigma_{\sigma'} \delta_{\sigma\sigma'}$ that arose when we transformed

$\psi_1^\dagger \psi_2^\dagger v(1,2) \psi_2 \psi_1$ into $\psi_1^\dagger \psi_1 v(1,2) \psi_2^\dagger \psi_2$. We omit this constant below, since it does not influence the physics. Let us rewrite the Hamiltonian in the representation of the functions $\phi_{jL}(\mathbf{r})$ (which can also be defined in different ways and we shall discuss it later). Using the expansion in Eq. (1) inserted into Eq. (5) gives

$$\mathcal{H} = \mathcal{H}_{nn} + \sum_{j_2L_2, j_3L_3} h^0_{j_2L_2, j_3L_3} a^\dagger_{j_2L_2} a_{j_3L_3} + \frac{1}{2} \sum_{\{jL\}} v^\dagger_{j_2L_2, j_3L_3, j_4L_4, j_5L_5} a^\dagger_{j_2L_2} a_{j_5L_5} a^\dagger_{j_3L_3} a_{j_4L_4}. \quad (7)$$

Here

$$h^0_{j_2L_2, j_3L_3} \equiv \left(j_2L_2 \left\| \left[\frac{p^2}{2m} - \sum_j \frac{Z_j e^2}{|\mathbf{r} - \mathbf{R}_j|} \right] \right\| j_3L_3 \right), \quad (8)$$

Now we assume that the nuclei are in fixed positions and separate the part of the Hamiltonian that contains on-site interactions between electrons that are treated as core electrons:

$$\mathcal{H}^{\text{ion}} = \sum_j \mathcal{H}_j^{\text{ion}} = \sum_j \left\{ \sum_{\mu_2, \mu_3} h^0_{j\mu_2, j\mu_3} f^\dagger_{j\mu_2} f_{j\mu_3} + \frac{1}{2} \sum_{\{\mu\}} v_{j\mu_2, j\mu_3, j\mu_4, j\mu_5} a^\dagger_{j\mu_2} a_{j\mu_5} a^\dagger_{j\mu_3} a_{j\mu_4} \right\}. \quad (9)$$

The single-site part of the problem and the rest will be treated in different approximations. We want to use Hubbard operators that are usually introduced in such a way that they diagonalize the single-ion Hamiltonian

$$H_j^{\text{ion}} |j, \Gamma_n\rangle = E_{j\Gamma_n} |j, \Gamma_n\rangle, \quad (10)$$

$$X_j^{\Gamma_n \Gamma_m} \equiv |j, \Gamma_n\rangle\langle j, \Gamma_m|. \quad (11)$$

Let us now discuss how to construct them.

B. The Hubbard operators in terms of fermions

We are not able to diagonalize the full Hamiltonian exactly, unless for certain model calculations, and we have to use some approximation. In order to ensure that the ground-state wave function fulfills Hund's rules, we will follow the technique by Irkhin and Irkhin,[13] who translated the Racah technique, used in atomic spectroscopy[14] for the wave functions, into the operator language. Although this issue has been discussed in Refs. 15 and 2, we find the definition used not fully satisfactory and in need of a slight modification. For this reason we discuss the definition of the many-electron operators and, correspondingly, the connection between the Hubbard operators and the many-electron creation and annihilation operators and the modification needed. The creation operator for a group of n equivalent electrons (say, in an f shell) in the many-electron state $|\Gamma_n\rangle = A^\dagger_{\Gamma_n}|0\rangle$ in the Irkhin-Irkhin definition has the form

$$A^\dagger_{\Gamma_n} = \frac{1}{\sqrt{n}} \sum_{\mu, \Gamma_{n-1}} G^{\Gamma_n}_{\Gamma_{n-1}} C^{\Gamma_n}_{\Gamma_{n-1}, \mu} f^\dagger_\mu A^\dagger_{\Gamma_{n-1}}. \quad (12)$$

Here $G^{\Gamma_n}_{\Gamma_{n-1}}$ are the fractional parentage coefficients, which do not depend on the momentum projections [if $n \leqslant 2$, $G = 1$ and the squared coefficient, $(G^{\Gamma_n}_{\Gamma_{n-1}})^2$, measures the fracture of the state $|\Gamma_{n-1}\rangle$ in $|\Gamma_n\rangle$]; $C^{\Gamma_n}_{\Gamma_{n-1}, \mu}$ are the Clebsch-Gordan coefficients

$$C^{\Gamma_n}_{\Gamma_{n-1}, \mu} \equiv C^{L_n M_L^{(n)}}_{L_{n\text{-}1} M_L^{(n-1)}, l m_l} C^{S_n M_S^{(n)}}_{S_{n-1} M_S^{(n-1)}, 1/2, \sigma}, \quad (13)$$

where $L_n, M_L^{(n)}, S_n$, and $M_S^{(n)}$ are the orbital moment, its projection, spin moment, and its projection for the n-electron configuration $|\Gamma_n\rangle$. In order to be able to calculate the commutation relations between the conduction electrons and the Hubbard operators as well as between the Hubbard operators themselves, we have to express them in terms of fermion operators. We have to provide the correct commutation relations for Hubbard operators, belonging to the same site

$$[X^{\gamma\Gamma}, X^{\Lambda\chi}]_\pm = \delta^{\Gamma\Lambda} X^{\gamma\chi} \pm \delta^{\chi\gamma} X^{\Lambda\Gamma}. \quad (14)$$

If we try to define a Hubbard operator in the form of a product of the operators A, i.e., $X^{\gamma\Gamma} = A^\dagger_\gamma A_\Gamma$, we should get zero if we multiply by $X^{\gamma\Gamma_n} X^{\Lambda_m \chi}$ for $n \neq m$. This should be provided by the fact that for the fermion operators $f^2 = (f^\dagger)^2 = 0$. However, the product $A_{\Gamma_n} A^\dagger_{\Lambda_m} \neq 0$, if $n < m$, because the operators A_{Γ_n} do not contain information about nonfilled orbitals of the shell. Therefore, the operators A_{Γ_n} do not provide the orthogonality of the states with different number of electrons in shell. The method suggested in Ref. 15 is to define new operators as follows:

$$\tilde{A}^\dagger_{\Gamma_n} = A^\dagger_{\Gamma_n} \prod_\mu (1 - \hat{n}_\mu), \quad \tilde{A}_{\Gamma_n} = \prod_\mu (1 - \hat{n}_\mu) A_{\Gamma_n}. \quad (15)$$

The product should run over all nonfilled orbitals. Let us consider, for example, the two-electron state composed of f states, $|\Gamma_2\rangle = |L = 5, M_L^{(2)} = 4, S = 1, M_S^{(2)} = 0\rangle$. Then, the operator

$$A^\dagger_{\Gamma_n} = \sum_{m_1 m_2 \sigma_1 \sigma_2} C^{5,4}_{3m_1, 3m_2} C^{1,0}_{1/2, \sigma_1; 1/2, \sigma_2} f^\dagger_{3m_1; 1/2, \sigma_1} f^\dagger_{3m_2; 1/2, \sigma_2} \quad (16)$$

combines three terms (for brevity below we omit indices $l = 3$ and spin $s = 1/2$):

$$A^\dagger_{\Gamma_2} = \alpha [f^\dagger_{3\uparrow} f^\dagger_{1\downarrow} + \gamma f^\dagger_{2\uparrow} f^\dagger_{2\downarrow} + f^\dagger_{1\uparrow} f^\dagger_{3\downarrow}] \quad (17)$$

with $\alpha = \sqrt{5/253}, \gamma = 27/\sqrt{15}$. Now, we have to multiply this by the product of the factors $(1 - \hat{n}_\mu)$, where μ runs over all empty orbitals. From this a problem is apparent: the different terms of the combinations of Clebsch-Gordan coefficients involve *different* orbitals, and therefore it is impossible to choose a single factor that includes all empty orbitals for each term in the sum. Therefore, *each term* of the sum must be supplemented with its own factor. In this particular example the new many-electron operator should be defined as follows:

$$\begin{aligned}\tilde{A}^{\dagger}_{\Gamma_2}=\alpha\Bigg[& f^{\dagger}_{3\uparrow}f^{\dagger}_{1\downarrow}\prod_{m_1\neq 3}(1-\hat{n}_{m_1\uparrow})\prod_{m_2\neq 1}(1-\hat{n}_{m_2\downarrow})\\ &+\gamma f^{\dagger}_{2\uparrow}f^{\dagger}_{2\downarrow}\prod_{m_1\neq 2}(1-\hat{n}_{m_1\uparrow})\prod_{m_2\neq 2}(1-\hat{n}_{m_2\downarrow})\\ &+f^{\dagger}_{1\uparrow}f^{\dagger}_{3\downarrow}\prod_{m_1\neq 1}(1-\hat{n}_{m_1\uparrow})\prod_{m_2\neq 3}(1-\hat{n}_{m_2\downarrow})\Bigg]\\ \equiv{}&\alpha[\tilde{A}^{\dagger}_{\Gamma_2(3\uparrow,1\downarrow)}+\gamma\tilde{A}^{\dagger}_{\Gamma_2(2\uparrow,2\downarrow)}+\tilde{A}^{\dagger}_{\Gamma_2(1\uparrow,3\downarrow)}].\end{aligned}\tag{18}$$

Obviously, in a general case, when we construct the operator $\tilde{A}^{\dagger}_{\Gamma_2}$, *each term* in the sum should be multiplied by the product of the factors $(1-\hat{n}_{m\sigma})$ corresponding to this term, where the set of $\{m\sigma\}$ includes only those orbitals that are not included in the product of the *f* operators in the corresponding term of the Clebsch-Gordan sum. Let us denote this product $\overline{\Pi}$, where the bar over Π means that it contains only complementary orbitals. In paper I we used the *orbital representation*, where each Hubbard operator contains only one term, containing *n* creation *f* operators for the *n*-electron state, which is multiplied by the product $\overline{\Pi}$. We will call it the *elementary operator*. In the case of Eq. (18) these operators are $\tilde{A}^{\dagger}_{\Gamma_2(3\uparrow,1\downarrow)}$, $\tilde{A}^{\dagger}_{\Gamma_2(2\uparrow,2\downarrow)}$, and $\tilde{A}^{\dagger}_{\Gamma_2(1\uparrow,3\downarrow)}$. We can, therefore, make the statement that any operator of a state in a central field (i.e., of the Clebsch-Gordan combination type) or in a crystal field can be represented as a sum of elementary operators with coefficients that are dictated by the symmetry of the surrounding of the ion. Since the construction of the state in central field within the Racah technique is recursive, i.e., the *n*-electron state is composed of $(n-1)$-electron states and one-electron states, the $(n-1)$-electron state is made of the combination of $(n-2)$- and one-electron states, and so on, this statement needs proof. Let us start with a many-electron operator, describing one localized electron in orbital 1. The electron state has the form $f^{\dagger}_1\Pi_{\nu\neq 1}(1-\hat{n}_{\nu})$. In order to construct the state, which contains two electrons localized in the states 1 and 2, we have to multiply this operator by $f^{\dagger}_2$ from the left-hand side. Since $f^{\dagger}_2(1-\hat{n}_2)=f^{\dagger}_2$, all extra factors $(1-\hat{n}_{\nu})$ are automatically projected out and we are back at Eq. (12). Therefore, each step to a higher number electron operator will be started again with Eq. (12). This means that the factors $\overline{\Pi}$ should be added in each term of the sum in the last step only. Thus, the Hubbard operator can be written in the form

$$X^{\gamma\Gamma}=\tilde{A}^{\dagger}_{\gamma}\tilde{A}_{\Gamma},\tag{19}$$

where each elementary operator entering the sum for the operator $\tilde{A}^{\dagger}_{\gamma}$ contains the projecting product $\overline{\Pi}^{(i)}_{\gamma}$. The same is valid for $\tilde{A}_{\Gamma}$ and $\overline{\Pi}^{(j)}_{\Gamma}$. Then, we can represent each $f_{j\mu}$ operator in any place where we meet it, particularly, in the Hamiltonian, in terms of Hubbard operators $X^{a}_{j}\equiv X^{a(\gamma,\Gamma)}_{j}\equiv X^{[\gamma,\Gamma]}_{j}$:

$$f_{j\mu}\equiv(f_{\mu})^{a}X^{a}_{j}.\tag{20}$$

Here, repeated indices are summed over. The Hubbard operators can also be written in the Hubbard form $X^{[\gamma,\Gamma]}_{j}\equiv|\mathbf{R}_j,n,\gamma\rangle\langle\mathbf{R}_j,n+1,\Gamma|$ or in terms of products of fermion operators as discussed above (here $|\mathbf{R}_j,n,\gamma\rangle$ and $|\mathbf{R}_j,n+1,\Gamma\rangle$ are many-electron *n*- and $(n+1)$-particle states). Using the definition of the many-electron operators and the Hubbard operators in terms of Fermion operators one can calculate all commutation relations between the conduction electrons operators and the Hubbard operators,[2]

$$\{c_{jL},X^{\bar{a}}_{j'}\}=\mathcal{O}^{-1}_{jL,j'\nu}f^{b}_{\nu}\varepsilon^{b\bar{a}}_{\xi}Z^{\xi}_{j'}.\tag{21}$$

Here, a,b denote the Fermi-like transitions from the *n*- to $(n+1)$-electron state $[a=a(\Gamma_n,\Gamma_{n+1})]$, $\bar{a}$ denotes the inverse transition $[\bar{a}=\bar{a}(\Gamma_{n+1},\Gamma_n)]$, $\xi=\xi(\Gamma_n,\Gamma'_n)$ and $\varepsilon^{b\bar{a}}_{\xi}$ are the structure constants of the algebra for the Hubbard operators,

$$\{X^{b}_{j},X^{\bar{a}}_{j}\}=\varepsilon^{b\bar{a}}_{\xi}Z^{\xi}_{j},\ \ \{X^{b}_{j},Z^{\xi}_{j}\}=\varepsilon^{b\xi}_{a}X^{a}_{j},\ \ \{X^{\bar{b}}_{j},Z^{\xi}_{j}\}=\varepsilon^{\bar{b}\xi}_{\bar{a}}X^{\bar{a}}_{j}.\tag{22}$$

The summation over repeating indices of transitions is implied. A Bose-like transition is denoted as Z^{ξ} and a diagonal Bose-like operator is denoted as h^{Γ}_{j}, $h^{\Gamma}_{j}\equiv Z^{\xi(\Gamma,\Gamma)}_{j}$.

C. The field for the electric potential and the Poisson equation

The full Coulomb interaction can be written as follows (see Ref. 6)

$$\begin{aligned}&\frac{1}{2}\int d\mathbf{q}[\hat{\rho}_i(\mathbf{q})-\hat{\rho}_{\mathbf{r}}(\mathbf{q})]\frac{4\pi e^2}{q^2}[\hat{\rho}_i(\mathbf{q})-\hat{\rho}_{\mathbf{r}}(\mathbf{q})]\\ &\equiv\frac{1}{2}\int d\mathbf{q}\,\hat{\rho}_{\mathbf{q}}\frac{4\pi e^2}{q^2}\hat{\rho}_{\mathbf{q}}.\end{aligned}\tag{23}$$

Here $\hat{\rho}_i(\mathbf{q})$ describes the nuclear densities screened by the core electrons

$$\hat{\rho}_i(\mathbf{q})=\sum_j\left(Z_j-\sum_{\xi}S^{\xi}_{j}(\mathbf{q})Z^{\xi}_{j}\right)e^{i\mathbf{q}\cdot\mathbf{R}_j},\tag{24}$$

and S^{ξ}_{j} is the form factor of the ion, which takes into account the contribution of the orbitals ν and μ into the transition ξ

$$S^{\xi}_{j}(q)=\int d\mathbf{r}\,e^{i\mathbf{q}\cdot\mathbf{r}}\phi^{*}_{j\nu}(\mathbf{r})\phi_{j\mu}(\mathbf{r})(f^{\dagger}_{\nu}f_{\mu})^{\xi};\tag{25}$$

the index *j* in $\phi_{j\mu}(\mathbf{r})$ denotes affiliation of this function to the ion on $\mathbf{R}_j$. All other electrons belong either to the class of the transitions between different ions, or to a mixed state between conduction and localized electrons, or to the conduction electrons. The operator of the charge density, $\hat{\rho}_{\mathbf{r}}(\mathbf{q})$, of these remaining electrons can be written as follows:

$$\hat{\rho}_{\mathbf{r}}(\mathbf{q})=\sum_{jLj'L'}\mathcal{O}jLj'L'(\mathbf{q})c^{\dagger}_{jL}c_{j'L'}+\sum_{jLj'L'}\mathcal{O}_{jLj'\mu'}(\mathbf{q})$$
$$\times(f_{\mu'})^{a}c^{\dagger}_{jL}X^{a}_{j'}+\mathcal{O}_{j\mu j'L'}(\mathbf{q})(f^{\dagger}_{\mu})^{\bar{a}}X^{\bar{a}}_{j}c_{j'L'}$$
$$+(1-\delta_{jj'})\mathcal{O}_{j\mu j'\mu'}(\mathbf{q})(f^{\dagger}_{\mu})^{\bar{a}}(f_{\mu'})^{b}X^{\bar{a}}_{j}X^{b}_{j'}\,. \tag{26}$$

The interaction between all nuclei that are screened by their electrons is

$$\frac{1}{2}\int d\mathbf{q}\,\hat{\rho}_i(\mathbf{q})\frac{4\pi e^2}{q^2}\hat{\rho}_i(-\mathbf{q})-\mathcal{H}_D\,. \tag{27}$$

Here, $\mathcal{H}_D$ takes into account the terms that are double counted in the first term, since there is no interaction of the ion with itself:

$$\mathcal{H}_D=\frac{1}{2}\sum_j\int d\mathbf{q}\left(Z_j-\sum_{\xi}S^{\xi}_j(\mathbf{q})Z^{\xi}_j\right)\frac{4\pi e^2}{q^2}$$
$$\times\left(Z_j-\sum_{\xi}S^{\xi}_j(\mathbf{q})Z^{\xi}_j\right). \tag{28}$$

The terms of this interaction at small **q**, as well as $\mathcal{H}_D$ itself, diverge. This is the standard problem of screening. The Hamiltonian in the many-electron representation is

$$\mathcal{H}=\mathcal{H}_0+(\mathcal{H}^{\mathrm{Coul}}+T), \tag{29}$$

where T is the kinetic energy, and the zero Hamiltonian is

$$\mathcal{H}_0=\mathcal{H}^{X}_0+\mathcal{H}^{c}_0=\sum_{j\Gamma}E^{\dagger}_{j\Gamma}h^{\Gamma}_j+\sum h^{0c}_{jL,j'L'}c^{\dagger}_{jL}c_{j'L'}\,. \tag{30}$$

Here $\mathcal{H}^{X}_0$ describes the electrons treated as core electrons when the interaction between the ions and all other electrons is switched off:

$$E_{j\Gamma}=\left(j,\Gamma\left|\sum_{i\in\mathbf{R}_j}\frac{p_i^2}{2m}-\sum_{i\in\mathbf{R}_j}\frac{Z_je^2}{|\mathbf{R}_j-\mathbf{r}_i|}\right.\right.$$
$$\left.\left.+\frac{1}{2}\sum_{i,i'\in\mathbf{R}_j}\frac{Z_je^2}{|\mathbf{r}_i-\mathbf{r}_{i'}|}\right|j,\Gamma\right). \tag{31}$$

The partition function, written in the standard form, is

$$Z=\mathrm{Tr}\exp[-\beta(\mathcal{H}-\mu N)]$$
$$=Z_0\frac{1}{Z_0}\mathrm{Tr}\left[\exp[-\beta\mathcal{H}_0]\mathcal{T}_{\tau}\exp\right.$$
$$\left.\times\left(-\int_0^{\beta}d\tau\,\mathcal{H}_{int}(\tau)\right)\right]$$
$$\equiv Z_0\left\langle\mathcal{T}_{\tau}\exp\left(-\int_0^{\beta}d\tau\,\mathcal{H}_{int}(\tau)\right)\right\rangle^{(0)}. \tag{32}$$

Let us write the part $\mathcal{H}^{\mathrm{Coul}}_{\rho\rho}$ of $\mathcal{H}_{\mathrm{int}}$ in the Fourier transformed form, Eq. (26). Then, we introduce the Gaussian functional integral

$$1=\int D\varphi_{\mathbf{q}}(\tau)\exp\left(-\int_0^{\beta}\frac{d\tau}{8\pi}\int d\mathbf{q}\;\;q^2\varphi_{\mathbf{q}}(\tau)\varphi_{-\mathbf{q}}(\tau)\right) \tag{33}$$

under the trace of the partition function. We make the shift

$$\varphi_{\mathbf{q}}(\tau)\rightarrow\varphi_{\mathbf{q}}(\tau)+i\frac{4\pi e}{q^2}\hat{\rho}_{\mathbf{q}}, \tag{34}$$

in this Gaussian integral. This allows us to rewrite the Coulomb interaction in terms of interaction of electrons with the random field $\varphi_{\mathbf{q}}(\tau)$. This shift generates the term $(-\mathcal{H}^{\mathrm{Coul}}_{\rho\rho})$, which cancels the $\mathcal{H}^{\mathrm{Coul}}_{\rho\rho}$ in $\mathcal{H}_{\mathrm{int}}$ but adds the term

$$-\frac{ie}{2}\int_0^{\beta}d\tau\int d\mathbf{q}\;\;[\varphi_{\mathbf{q}}(\tau)\hat{\rho}_{-\mathbf{q}}(\tau)+\hat{\rho}_{\mathbf{q}}(\tau)\varphi_{-\mathbf{q}}(\tau)]. \tag{35}$$

Note that, although the f orbitals of the same site are orthogonalized, the $\mathbf{q}\neq 0$ components of the overlap matrix have nonzero values and, therefore, nondiagonal transitions $\xi\neq[\Gamma,\Gamma]$ enter the expression for **q** component of the charge density. Thus, we have to work with the following expression for the partition function:

$$\frac{Z}{Z_0}=\int D\varphi_{\mathbf{q}}(\tau)\exp\left(-\int_0^{\beta}d\tau\int d\mathbf{q}\;\;\frac{q^2}{8\pi}\varphi_{\mathbf{q}}(\tau)\varphi_{-\mathbf{q}}(\tau)\right)$$
$$\times\exp\{-\beta\mathcal{F}_i[\varphi_{\mathbf{q}}(\tau),\varphi_{-\mathbf{q}}(\tau)]\}, \tag{36}$$

where

$$\mathcal{F}_i[\varphi_{\mathbf{q}}(\tau),\varphi_{-\mathbf{q}}(\tau)]$$
$$\equiv-\frac{1}{\beta}\ln\left\langle\mathcal{T}_{\tau}\exp\left(-\int_0^{\beta}d\tau\int d\mathbf{q}(T_{\mathbf{q}}-\mathcal{H}_{\rho}-\mathcal{H}_D)\right)\right\rangle^{(0)}, \tag{37}$$

$$T_{\mathbf{q}}\equiv\left[\frac{\hat{p}^2}{2m}\right]_{\mathbf{q}}\rho_{\mathbf{r}}(\mathbf{q}), \tag{38}$$

$$\mathcal{H}_{\rho}=\frac{1}{2}\int d\mathbf{q}\;\;[ie\varphi_{\mathbf{q}}(\tau)-\mu]\hat{\rho}_{-\mathbf{q}}(\tau)+\hat{\rho}_{\mathbf{q}}(\tau)[ie\varphi_{-\mathbf{q}}(\tau)-\mu], \tag{39}$$

$$\mathcal{H}^{0}_{i}=\mathcal{H}^{c}_{0}+\mathcal{H}^{X}_{0}\,. \tag{40}$$

Here, we have used the fact that the fields $\varphi_{\mathbf{q}}(\tau)$ commute with any operator. The function $\mathcal{F}$ is written in the form usually used for the cumulant expansion.

Since both the mixing interaction and overlap matrices are nonzero, a part of the charge is in the mixed cf states. Besides, the f subsystem is described in terms of *nonlinear X* operators. For these reasons we cannot describe the full contribution from the term $\mu\hat{N}$ in the zero Hamiltonian. The field $\varphi_{\mathbf{q}}(\tau)$ can be interpreted as the field for the electrical potential that is generated by the Coulomb interaction. If we set $e=0$ the system does not have charged particles, and therefore there is no contribution to the partition function from this field. At $e\neq 0$ in a nonhomogeneous system an average charge density is not equal to zero, and, therefore, the expectation value $\langle \varphi_{\mathbf{q}}(\tau)\rangle_{\varphi}$ is nonzero too. Taking the functional derivative of the free energy, we find that the saddle-point approximation generates the Poisson equation for this field:

$$\frac{\delta F}{\delta\varphi_{-\mathbf{q}}(\tau)} \equiv \frac{\delta(-\mathcal{T}\ln Z)}{\delta\varphi_{-\mathbf{q}}(\tau)} = -\frac{q^2}{8\pi}\langle \varphi_{\mathbf{q}}(\tau)\rangle_{\varphi} + \frac{ie}{2}\langle \hat{\rho}_{\mathbf{q}}(\tau)\rangle_{\varphi} = 0. \tag{41}$$

The static part of the field of the electrical potential $\Phi(\mathbf{r})$ is connected with the field $\langle\varphi\rangle$ as follows:

$$\Phi(\mathbf{r}) \equiv \lim_{\tau\to -0} i\langle \varphi(\mathbf{r},\tau)\rangle_{\varphi} = i\langle \varphi(\mathbf{r},0)\rangle_{\varphi}. \tag{42}$$

Thus, we have the Poisson equation for the electric potential $\Phi(\mathbf{r})$,

$$\nabla^2\Phi(\mathbf{r}) = -4\pi\langle \hat{\rho}_{\mathbf{q}}(0)\rangle_{\varphi}, \tag{43}$$

where the charge density is the difference between the densities of the delocalized electrons and the "soft" ion (where the polarization of the ion and excitations are allowed).

III. THE SELF-CONSISTENT HUBBARD-ANDERSON MODEL

The field $\varphi(\mathbf{r},\tau)$ contains the average static field and deviations of it:

$$\varphi(\mathbf{r},\tau) = \frac{1}{i}\Phi(\mathbf{r}) + \delta\varphi(\mathbf{r},\tau). \tag{44}$$

It is reasonable to start with the approximation $i\varphi_{\mathbf{q}}(\tau) \to i\langle \varphi_{\mathbf{q}}(0)\rangle_{\varphi} \to \Phi(\mathbf{q})$, and to neglect the fluctuations of this field. Then, we obtain the following saddle-point Hamiltonian:

$$\tilde{\mathcal{H}}_0 = \int d\mathbf{q}\;\; q^2\Phi(\mathbf{q})\Phi(-\mathbf{q}) + \sum\, (h_{jL,j'L'} - \mu\,\mathcal{O}_{jL,j'L'}) \times c^{\dagger}_{jL}c_{j'L'} + \sum\, (E^{(n)}_{j\Gamma} - n\mu)h^{\Gamma}_{j}, \tag{45}$$

$$\tilde{\mathcal{H}}_{int} = T + \frac{e}{2}\int d\mathbf{q}\;\; [\Phi(\mathbf{q})\hat{\rho}_{-\mathbf{q}} + \hat{\rho}_{\mathbf{q}}\Phi(-\mathbf{q})] - \mathcal{H}_D. \tag{46}$$

Here

$$h_{jL,j'L'} = \left(jL \left| \frac{\hat{p}^2}{2m} + \Phi(\mathbf{r}) \right| j'L' \right) \tag{47}$$

is the frequency matrix of the conduction electrons in the self-consistent field $\Phi(\mathbf{r})$. The Hamiltonian $\tilde{\mathbf{h}}$ for them can be obtained if we make a transformation to the orthogonal variables $\boldsymbol{\alpha}$, using the Cholesky decomposition for the overlap matrix $\mathbf{O}$:

$$\begin{aligned}\mathbf{c}^{\dagger}(\mathbf{h} - \mu\,\mathbf{O})\mathbf{c} &= \mathbf{c}^{\dagger}[\overline{\mathbf{Z}}(\overline{\mathbf{Z}}^{-1}\mathbf{h}\mathbf{Z}^{-1})\mathbf{Z} - \mu\overline{\mathbf{Z}}\mathbf{Z}]\mathbf{c} \\ &= (\mathbf{c}^{\dagger}\overline{\mathbf{Z}})[\tilde{\mathbf{h}} - \mu\mathbf{I}](\mathbf{Z}\mathbf{c}) = \alpha^{\dagger}[\tilde{\mathbf{h}} - \mu\mathbf{I}]\alpha.\end{aligned} \tag{48}$$

Let us now insert into $\tilde{\mathcal{H}}_{\rm int}$ the expression for $\hat{\rho}_{\mathbf{q}}$ in the jL-representation. Taking into account that

$$\frac{e}{2}\int d\mathbf{q}\;\; \Phi(\mathbf{q})\mathcal{O}_{jL,j'L'}(\mathbf{q}) = \frac{e}{2}\int d\mathbf{r}\;\; \phi^{*}_{jL}(\mathbf{r})\Phi(\mathbf{r})\phi_{j'L'}(\mathbf{r}) \equiv V_{jL,j'L'} \tag{49}$$

are matrix elements of the self-consistent Coulomb field, we find that $\tilde{\mathcal{H}}$ actually gives the periodic Hubbard-Anderson Hamiltonian

$$\begin{aligned}\tilde{\mathcal{H}} = &\int d\mathbf{q}\;\; q^2\Phi(\mathbf{q})\Phi(-\mathbf{q}) \\ &+ \sum\, (h^{\rm LDA} - \mu\,\mathcal{O})_{jL,j'L'}c^{\dagger}_{jL}c_{j'L'} + \sum\, (\tilde{E}^{(n)}_{j\Gamma} - n\mu)h^{\Gamma}_{j} \\ &+ \sum \Bigg[V_{j\mu,j\mu'}(f^{\dagger}_{\mu}f_{\mu'})^{\xi\neq[\Gamma,\Gamma]}Z^{\xi} + \text{H.c.} \\ &+ \sum \left(\frac{p^2}{2m} + V - \mu\mathcal{O}\right)_{jL,j'\mu'} (f_{\mu'})^{a}c^{\dagger}_{jL}X^{a}_{j'} \\ &+ \left(\frac{p^2}{2m} + V - \mu\mathcal{O}\right)_{j\mu,j'\mu'} (f^{\dagger}_{\mu})^{\bar{a}}X^{\bar{a}}_{j}c_{j'L}\Bigg] \\ &+ \sum\, (1 - \delta_{jj'})\left(\frac{p^2}{2m} + V - \mu\mathcal{O}\right)_{j\mu,j'\mu'} \\ &\times (f^{\dagger}_{\mu})^{\bar{a}}(f_{\mu'})^{b}X^{\bar{a}}_{j'}X^{b}_{j'} - \mathcal{H}_D.\end{aligned} \tag{50}$$

Thus, within this approximation, the single-ion energies $\tilde{E}^{(n)}_{j\Gamma}$ are shifted by the self-consistent field of interaction with other ions, delocalized electrons and the localized ones, but belonging to other sites: $\tilde{E}^{(n)}_{j\Gamma} = E^{(n)}_{j\Gamma} + \langle\Gamma|\Phi(r)|\Gamma\rangle$. However, the self-consistent field should be found from the Poisson equation, and therefore it contains only the Hartree part of the interaction between the collective quasiparticles. Nevertheless, this problem does not coincide with the single-particle Hartree approximation, since it contains additional information about the structure of the many-electron states $|\Gamma\rangle$ of the ion. Due to the nonlinearity of the problem the approximations for the Green functions (GF's) can be used in a different form from the standard single-particle problem in the Hartree approximation. Particularly, as seen from the solution of the self-consistent Anderson model, presented in Ref. 16, the potential depends implicitly on the many-body population numbers of the ion states already in the lowest approximation.

The exchange contribution appears in first order between electrons via the fluctuation of the field $\varphi \propto \langle \mathcal{T}\delta\varphi(\tau)\delta\varphi(\tau')\rangle$. This study we leave for the future, however, it is interesting to note that this exchange involves also the contributions from fluctuations caused by the intra-ion transitions.

The charge density and the averages $\langle c^{\dagger}_{jL}c_{j'L'}\rangle$, $\langle c^{\dagger}_{jL}X^{a}_{j'}\rangle$, $\langle X^{\bar{a}}_{j'}c_{jL}\rangle$, $\langle X^{\bar{a}}_{j}X^{b}_{j'}\rangle$, for the Poisson equation can be found from the GF's. It is clear that if it is possible to approximate this potential by a spherically symmetrical one, $V_{j\mu j\mu'}=\delta_{\mu\mu'}V_j$, then $(f^{\dagger}_{\mu}f_{\mu})^{\xi}=\delta_{\xi,[\Gamma,\Gamma]}$ for the orbitals, μ, occupied in the state Γ.

IV. MIXING INTERACTION

Let us now rewrite the problem in a form close to the standard periodical Anderson model. This allows us to discuss different possible definitions for the matrix element of the mixing interaction. Usually the Hamiltonian of the Anderson model is written in the following form:

$$\mathcal{H}^{(\mathrm{And})}=\sum_{\mathbf{k}\sigma}\varepsilon^{\sigma}_{\mathbf{k}}c^{\dagger}_{\mathbf{k}\sigma}c_{\mathbf{k}\sigma}+\sum_{\mathbf{k}\sigma}[V^{\sigma}_{\mathbf{k}\mu}e^{i\mathbf{k}\cdot\mathbf{R}_j}c_{\mathbf{k}\sigma^{\dagger}}f_{j\mu}+\mathrm{H.c.}$$

$$+\sum_{j\{\mu\}}U_{\mu_1\mu_2\mu_3\mu_4}f^{\dagger}_{j\mu_1}f^{\dagger}_{j\mu_2}f_{j\mu_3}f_{j\mu_4}+\sum_{j\mu}\epsilon_{\mu}f^{\dagger}_{j\mu}f_{j\mu}. \tag{51}$$

Here $\varepsilon^{\sigma}_{\mathbf{k}}$ is the spectrum of the conduction electrons, $V^{\sigma}_{\mathbf{k}\mu}$ is the matrix element of mixing interaction,

$$V^{\sigma}_{\mathbf{k}\mu}=\int d\mathbf{r}\,\phi^{*\sigma}_{\mathbf{k}}(\mathbf{r})\left(\frac{p^2}{2m}+V(\mathbf{r})\right)\varphi_{\mu}(\mathbf{r}-\mathbf{R}_j), \tag{52}$$

and $U_{\mu_1\mu_2\mu_3\mu_4}$ is the matrix elements of the Coulomb intrashell interactions. For the mixing no problem arises in the case of the impurity Anderson model, since the potential in this case is the difference between the periodical potential for the conduction electrons and the potential of the impurity, although the local on-site term is equal to zero due to symmetry reasons, overlap with the orbitals of neighboring ions gives a nonzero contribution (see the paper by Anderson[17]). In the case of the periodic Anderson model (PAM) this form of the matrix element suggests that either the potential has different symmetry from the Bloch wave functions, or the functions $\phi^{*\sigma}_{\mathbf{k}}(r)$ and $\varphi_{\mu}(\mathbf{r}-\mathbf{R}_j)$ are not orthogonal. It is not clear how to fulfill the first assumption in the case of elemental metals (like Ce metal) since we are dealing with a periodic system. In the second case

$$\int d\mathbf{r}\,\phi^{*\sigma}_{\mathbf{k}}(\mathbf{r})\left(\frac{p^2}{2m}+V(\mathbf{r})\right)\varphi_{\mu}(\mathbf{r}-\mathbf{R}_j)$$

$$=\varepsilon^{\sigma}_{\mathbf{k}}\int d\mathbf{r}\,\phi^{*\sigma}_{\mathbf{k}}(\mathbf{r})\varphi_{\mu}(\mathbf{r}-\mathbf{R}_j)=\varepsilon^{\sigma}_{\mathbf{k}}\mathcal{O}_{\mathbf{k}\sigma,j\mu}. \tag{53}$$

Therefore, in order to have a nonzero mixing, one has to work in terms of a nonorthogonal basis set, but in this case (a) there is a contribution from the chemical potential to the partition function that affects the mixing, and (b) the nonorthogonality causes nonzero anticommutation relations between the *f* and *c* operators. This is never taken into account in model calculations.

Let us consider the consequences from our formulation. Since the mixing matrix element has a single-electron form, let us make in our saddle-point Hamiltonian a transformation that diagonalizes the conduction electrons. First we have to rewrite the Hamiltonian, Eq. (50) in **k** space (for the formulas to be transparent, we will write them for the case of one atom in the elementary cell, then, the single-ion matrix elements and energies do not depend on the ion index). The Hamiltonian is written using the new variables:

$$c_{jL}=\sum_{\mathbf{k}}e^{-i\mathbf{k}\cdot\mathbf{R}_j}c_{\mathbf{k}L},\quad c^{\dagger}_{jL}=\sum_{k}e^{i\mathbf{k}\cdot\mathbf{R}_j}c^{\dagger}_{\mathbf{k}L}, \tag{54}$$

We want to decompose the overlap matrix,

$$\mathbf{c}^{\dagger}(\mathbf{h}-\mu\mathbf{O})\mathbf{c}=\mathbf{c}^{\dagger}[\overline{\mathbf{Z}}(\overline{\mathbf{Z}}^{-1}\mathbf{h}\mathbf{Z}^{-1})\mathbf{Z}-\mu\overline{\mathbf{Z}}\mathbf{Z}]\mathbf{c}$$

$$=(\mathbf{c}^{\dagger}\overline{\mathbf{Z}})[\tilde{\mathbf{h}}-\mu\mathbf{I}](\mathbf{Z}\mathbf{c})=\boldsymbol{\alpha}^{\dagger}[\tilde{\mathbf{h}}-\mu\mathbf{I}]\alpha, \tag{55}$$

this introduces transformed operators $\alpha_{\mathbf{k}\gamma}=Z^{\gamma L}_{\mathbf{k}}c_{\mathbf{k}L}$, $\alpha^{\dagger}_{\mathbf{k}\gamma}=c^{\dagger}_{\mathbf{k}L}\overline{Z}^{L\gamma}_{\mathbf{k}}$. It is easy to see that they are orthogonal to each other:

$$\alpha_{\mathbf{k}\gamma}\alpha^{\dagger}_{\mathbf{k}\gamma'}+\alpha^{\dagger}_{\mathbf{k}\gamma'}\alpha_{\mathbf{k}\gamma}=Z^{\gamma L}_{\mathbf{k}}(c_{\mathbf{k}L}c^{\dagger}_{\mathbf{k}L'}+c^{\dagger}_{\mathbf{k}L'}c_{\mathbf{k}L})\overline{Z}^{L'\gamma'}_{\mathbf{k}}$$

$$=Z^{\gamma L}_{\mathbf{k}}(\mathcal{O}^{-1})_{LL'}\overline{Z}^{L'\gamma'}_{\mathbf{k}}$$

$$=Z^{\gamma L}_{\mathbf{k}}(Z^{-1}_{\mathbf{k}})^{L\gamma_1}(\overline{Z}^{-1})^{\gamma_1 L'}\overline{Z}^{L'\gamma'}_{\mathbf{k}}=\delta_{\gamma\gamma'}. \tag{56}$$

At last, diagonalizing the conduction-electron Hamiltonian $\overline{\mathbf{Z}}^{-1}\mathbf{h}\mathbf{Z}^{-1}$, we have

$$\tilde{\mathcal{H}}=\int d\mathbf{q}\;q^2\Phi(\mathbf{q})\Phi(-\mathbf{q})+\sum[\varepsilon_{\mathbf{k}\lambda}-\mu]\tilde{c}^{\dagger}_{\mathbf{k}\lambda}\tilde{c}_{\mathbf{k}\lambda}$$

$$+\sum(\tilde{E}^{(n)}_{\Gamma}-n\mu)h^{\Gamma}_{j}+\sum[V_{\mu,\mu'}(f^{\dagger}_{\mu}f_{\mu'})^{\xi\neq[\Gamma,\Gamma]}Z^{\xi}_{j}$$

$$+\mathrm{H.c.}]+\sum[V^{\overline{a}}_{\lambda}(k)e^{i\mathbf{k}\cdot\mathbf{R}_j}\tilde{c}^{\dagger}_{\mathbf{k}\lambda}X^{a}_{j'}+\mathrm{H.c.}]+\sum(1-\delta_{jj'})$$

$$\times\left(\frac{p^2}{2m}+V-\mu\mathcal{O}\right)_{j\mu,j'\mu'}$$

$$\times(f^{\dagger}_{\mu})^{\overline{a}}(f_{\mu'})^{b}X^{\overline{a}}_{j}X^{b}_{j'}-\mathcal{H}_D, \tag{57}$$

where the band energy and mixing matrix elements are

$$\varepsilon_{\mathbf{k}\lambda}=\vartheta^{*\lambda}_{\gamma}(\mathbf{k})(\overline{Z}^{-1}_{\mathbf{k}})^{\gamma L}h_{L,L'}(\mathbf{k})(Z^{-1}_{\mathbf{k}})^{L\gamma'}\vartheta^{\lambda}_{\gamma'}(\mathbf{k}), \tag{58}$$

$$V^{\overline{a}}_{\lambda}(\mathbf{k})=\vartheta^{*\lambda}_{\gamma}(\mathbf{k})(\overline{Z}^{-1})^{\gamma L}\left(\frac{p^2}{2m}+V-\mu\mathcal{O}\right)_{jL,j'\mu'}(f_{\mu'})^{a}$$

$$\equiv v^{\lambda}_{\mu'}(\mathbf{k})(f_{\mu'})^{a}, \tag{59}$$

$$V^{*\overline{a}}_{\lambda}(\mathbf{k})=\left(\frac{p^2}{2m}+V-\mu\mathcal{O}\right)_{j\mu,j'L}(Z^{-1}_{\mathbf{k}})^{L\gamma}\theta^{\lambda}_{\gamma}(\mathbf{k})(f^{\dagger}_{\mu})^{\overline{a}}$$

$$\equiv(f^{\dagger}_{\mu})^{\overline{a}}v^{*\lambda}_{\mu'}(\mathbf{k}), \tag{60}$$

where $\{\vartheta\}$ diagonalizes $\overline{\mathbf{Z}}^{-1}\mathbf{h}\mathbf{Z}^{-1}$, and v^{λ}_{i} is the one-electron hybridization parameter. Thus, the matrix element of the mixing interaction has to be found self-consistently together with the charge density (which in turn depends on the particular approximation in which the PAM is solved) and can be represented in the form of a sum over all localized

TABLE I. Coefficients for the mixing interaction for many-body states. For the *f* series, taken from Ref. 15.

n	1	2	3	4	5	6	7	8	9	10	11	12	13	14
$[f_{5/2}]^2$	1	2.25	2.3	1.8	0.9	0.15	0	1.6	2.3	4.1	1.7	0.9	0.3	0
$[f_{7/2}]^2$	0	0.25	0.6	0.8	0.63	0	0.9	0.5	1.3	4.1	3.0	3.3	2.8	1

orbitals of products of the matrix element of the single-particle potential [on the conduction-electron Bloch function $\phi_{k\lambda}(\mathbf{r})$ and the localized orbital $\chi_\mu(\mathbf{r})$] and the factor $(f_{\mu'})^a$, which reflects the contribution of this orbital into a fermionlike transition. Irkhin and Irkhin[15] have performed the calculation of this factor for the $4f$ elements, making use of the Racah technique leaving the single-particle matrix element undefined. Setting $\overline{a}=\overline{a}(\Gamma_n,\Gamma_{n-1})$ and $\mu=(l,m,\sigma)$ and using the result of the calculation of Irkhin and Irkhin, we can write these coefficients as follows:

$$(f^\dagger_\mu)^{\overline{a}}=\langle\Gamma_n|f^\dagger_{lm\sigma}|\Gamma_{n-1}\rangle$$

$$=\sqrt{n[\Gamma_n][\Gamma_{n+1}]}\begin{Bmatrix} S_n & L_n & J_n \\ S_{n-1} & L_{n-1} & J_{n-1} \\ 1/2 & l & j \end{Bmatrix} G^{\Gamma_n}_{\Gamma_{n-1}}, \tag{61}$$

where $\gamma=(lm_l\sigma)$ are the one-electron quantum numbers, $[a]=2a+1$ and $G^{\Gamma_n}_{\Gamma_{n-1}}$ is the parentage Racah coefficients and $j=l+1/2$. The coefficients $(f^\dagger_\mu)^{\overline{a}}$ are different for the two channels, $j=5/2$ and $j=7/2$. The square of these coefficients are given in Table I.

However, there are more considerations to the problem, since the Bloch orbitals are not orthogonal to the localized orbitals. In the equation of motion for the operators appear combinations involving the overlap matrices. For the Hamiltonian, which includes hopping and mixing interactions (the periodic Hubbard-Anderson model), the diagram technique and different approximations for the Green functions (GF) are given in paper I, while the full self-consistent solution for rare earths in the simplest possible approximation is presented in Ref. 16.

V. DISCUSSION

Many different suggestions exist in the literature on how the parameters of the Anderson Hamiltonian (periodical or impurity) should be calculated from an *ab initio* approach and a consensus is not yet achieved. This motivated us to make an attempt to derive the parameters from a total Hamiltonian. Since the Anderson model is usually used for the description of the cases when strong electron correlations are well developed, it is reasonable to consider strong intra-atomic Coulomb interactions first. For this reason we have performed a derivation of the self-consistent PAM in four steps: (i) first we separate, in the Hamiltonian, the strong intra-atomic interactions and approximately diagonalized them with the help of many-electron functions describing different ion terms; (ii) we expressed all operators, describing *f* and core electrons in terms of Hubbard operators; (iii) we performed the Hubbard-Stratonovich decoupling of the Coulomb interaction, and finally (iv) we found the equation for the electric potential in a saddle-point approximation. This lead us to the effective Hamiltonian, which coincide with the generalized PAM.

All three operations before making the saddle-point approximation are exact. However, the saddle-point approximation neglects the contributions from the exchange interaction for the delocalized particles (excitations) and Coulomb screening effects, which appear only in the next orders with respect to fluctuations of this field near its saddle-point value. Thus, we may conclude that from this point of view this model is quite rough. On the other hand, the way suggested here has an obvious advantage compared to the PAM with non-self-consistent parameters since it, at least, takes care about perturbations of the local charge density which may introduce quite large changes in energy.

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