Electronic structure and energetics of praseodymium and α-plutonium under pressure

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We develop a new implementation of the Gutzwiller approximation (GA) and interface it with the local density approximation (LDA). This formulation enables us to study complex 4f and 5f systems. We perform calculations of praseodymium and α-plutonium under pressure, which compare very well with the experiments. Our study of praseodymium indicates that both structure change and f-delocalization are important to obtain the correct phase diagram and, in particular, the pressure-induced volume-collapse transition. Our calculations of α-plutonium indicate that, even though the f electrons are delocalized in this phase, the electron-correlations affect substantially its electronic structure and thermodynamical properties.

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I. INTRODUCTION

There has been a renewed interest in first-principles approaches to the electronic structure of strongly correlated materials. The density functional theory (DFT) proved to be a good starting point for deriving model Hamiltonians, and was taken as a starting point for more elaborated methods to treat correlations. While early approaches to solve the realistic many-body problem in solids focused on perturbative treatments of the interactions over the last two decades several non-perturbative methodologies have emerged. Dynamical mean field theory (DMFT) was combined with realistic electronic structure methods, for example in the LDA+DMFT approach. This methodology can be thought as a spectral density functional and is nowadays widely used to treat ground state and spectral properties at zero and finite temperatures of 3d, 4d, 5d, 4f and 5f systems. For reviews see, e.g., Refs. 18–20.

LDA+DMFT has been implemented in different basis sets, such as linearized augmented planewave (LAPW), plane wave pseudopotential, projector augmented wave method and linearized muffin-tin orbital. Another important approach is the GA which was first implemented to study real solids in Ref. 21. The GA approximation has been thereafter extensively developed and it has been formulated and implemented in combination with realistic electronic structure calculations such as the LDA+GA approach, which has been applied successfully to many systems. A third important many-body technique is the slave boson approach, which is, in principle, an exact reformulation of the quantum many-body problem for model Hamiltonians, and reproduces the results of the GA at the saddle-point level. This technique has been recently extended to treat full rotationally-invariant interactions and has also been successfully combined with LDA for the study of real materials. The so-obtained LDA + slave bosons approach is fully equivalent to the LDA+GA method. The goal of this paper is three-fold. (I) On the methodological side, we show that the three above-mentioned methods are actually closely connected, and largely complementary of each other. We use the connection between the GA and the slave-boson method to introduce a functional formulation, which can be used not only at zero temperature, but also at finite (low) temperatures. This functional is a first step toward deriving formulae for the forces and the phonon spectra in the LDA+GA and LDA+slave boson methods. Our functional formulation of the LDA+GA method has a mathematical structure similar to LDA+DMFT. This parallelism suggests possible synergistic combinations between the two methods — such as using LDA+GA for structural relaxation while using the exact impurity solver in the LDA+DMFT iteration to determine the spectral properties. Furthermore, it enables us to pattern the LAPW interface between LDA and the GA after the LDA+DMFT work of Ref. (II) On the algorithmic side, these connections result in a new algorithm for solving the LDA+GA equations, which is faster and more precise than earlier methods, and that sheds light on the interpretation of the slave-boson amplitudes — which are central quantities both in the GA and in the slave-boson approach. In fact, we display a connection between the above-mentioned parameters and the coefficients of the Schmidt decomposition — that was recently used also to derive the density matrix embedding theory (DMET). Our reformulation of the GA problem consists in solving recursively ground-state calculation of a series of Anderson impurity Hamiltonians (one for each inequivalent impurity within the lattice unit cell), whose baths have the same dimension as the corresponding impurities. Our algorithm enables us to derive accurate equations of state for materials currently far beyond the reach of the LDA+DMFT method. (III) These advances result in a new understanding of the volume-collapse transition in f systems. In particular, we use our...
all-electron (LAPW) implementation of the LDA+GA method to study two prototypical systems with partially delocalized \( f \) electrons: the elemental praseodymium and the \( \alpha \) allotrope of plutonium. Praseodymium is a rare-earth as cerium, and follows it in the periodic table. An interesting property of the elemental praseodymium is that, similarly to many other rare-earths compounds, it undergoes a volume-collapse structure-transition under pressure, which is accompanied by an abrupt delocalization of the \( f \)-electrons. Here we compute its pressure-volume phase diagram, finding very good agreement with the experiments. In particular, we show that the method is able to capture the pressure-induced volume-collapse structure-transition toward the low-symmetry \( \alpha \)-U phase, and that the GA correction to the total energy is crucial to determine correctly the stable lattice structure of praseodymium. Finally, we investigate the relation between the \( f \)-delocalization and the volume-collapse structure-transition — which is one of the most important puzzles in condensed matter physics. Our conclusion is that, contrarily to cerium, in praseodymium there would not be any volume-collapse transition without taking into account the change of lattice structure (at least at small temperatures). The stable allotrope of plutonium at ambient conditions — and consequently the most common on earth — is \( \alpha \)-Pu. As pointed out in a recent theoretical study using DMFT in combination with the generalized gradient approximation (GGA), see Ref. 51 the low lattice-symmetry of \( \alpha \)-Pu originates site-selective electronic correlations, which make the electronic structure of this allotrope very interesting and complex, as well as very difficult to study theoretically. Here we describe in detail the zero-temperature electronic structure of \( \alpha \)-Pu and calculate its pressure-volume phase diagram, finding very good agreement with the experiments. Furthermore, we discuss the role of the electron-correlations and their dependence on the applied pressure. The outline of the paper is as follows. In Sec. II the formulation and the implementation of the GA developed in Refs. 22-29 is substantially improved. Furthermore, the connection between the GA variational parameters and the coefficients of the Schmidt decomposition is discussed. In Sec. III the connection between the GA and DMFT is discussed. In Sec. IV our functional formulation of the LDA+GA method is derived. In order to make the exposition more clear, each of these sections conclude with a short summary of the main results. Finally, in Secs. V and VI our calculations of praseodymium and \( \alpha \)-plutonium are illustrated.

II. THE GUTZWILLER APPROXIMATION FOR THE HUBBARD MODEL

Let us consider the Hubbard model (HM)

\[
\hat{H} = \sum_k \sum_{ij} \epsilon_{k,ij} c_{k\alpha}^\dagger c_{k\beta} + \sum_{R\alpha} \hat{H}_{R\alpha}^{\text{loc}} \{ \hat{c}_{R\alpha}^\dagger, \{ \hat{c}_{R\alpha} \} \};
\]

where \( k \) is the momentum conjugate to the unit-cell label \( R \), the atoms within the unit cell are labeled by \( i, j \), and the spin-orbitals are labeled by \( \alpha, \beta \). We assume that the first term is non-local, i.e., that

\[
\sum_k \epsilon_{k,ii} = 0 \quad \forall i,
\]

and that \( \hat{H}^{\text{loc}} \) includes both the one-body and the two-body part of the Hamiltonian.

The Gutzwiller method consists in determining variationally a projected wavefunction represented as

\[
|\Psi_G\rangle = \hat{P}_G |\Psi_0\rangle \equiv \prod_{Ri} \hat{P}_{Ri} |\Psi_0\rangle,
\]

where \( |\Psi_0\rangle \) is a Slater determinant and \( \hat{P}_{Ri} \) is an operator acting on the local configurations at the site \( (R, i) \).

In order to evaluate analytically the expectation value of \( \hat{H} \) with respect to \( |\Psi_G\rangle \), two further approximations are done on top of Eq. (3). (1) The manifold of variational wavefunctions is further restricted by the following condition,

\[
\langle \Psi_0 | \hat{P}_{Ri}^\dagger \hat{P}_{Ri} |\Psi_0\rangle = 1
\]

\[
\langle \Psi_0 | \hat{P}_{Ri}^\dagger \hat{P}_{R\alpha} \hat{c}_{R\alpha}^\dagger \hat{c}_{R\beta} |\Psi_0\rangle = \langle \Psi_0 | \hat{c}_{R\alpha}^\dagger \hat{c}_{R\beta} |\Psi_0\rangle
\]

which are commonly named “Gutzwiller constraints”.

(2) The so called GA is assumed, which is an approximation scheme that, as DMFT becomes exact in the limit of infinite coordination lattices, see, e.g., Ref. 23.

A. Lagrange formulation of the GA

As shown in Refs. 25-29 and demonstrated here in the Appendix A for completeness, the GA problem can be formulated in terms of the following Lagrange-function, which is the starting point of this work, and gives the ground-state total energy when it is evaluated on its saddle-point:
\[
\mathcal{L}_N[\Psi_0, E; \phi, E^c; \mathcal{R}, \mathcal{R}^\dagger, \lambda, \eta, \mu; D, D^\dagger, \lambda^c; n^c] = \frac{1}{N} \langle \Psi_0 | \hat{H}_G^{\text{pp}}(\mathcal{R}, \mathcal{R}^\dagger; \lambda + \eta; \mu) | \Psi_0 \rangle + E(1-\langle \Psi_0 | \Psi_0 \rangle) + \\
\sum_{k, \mathcal{R}} \text{Tr} \left[ \phi_i \phi_i^\dagger \hat{H}_G^{\text{loc}} \right] + \sum_{a, \alpha} \left[ (D_{\mathcal{R} a}^\dagger \phi_i^\dagger F_{i a} \phi_i + \text{H.c.}) + \sum_{a b} [\lambda_i^\dagger]_{a b} \phi_i^\dagger F_{a b}^\dagger F_{i b} \right] + \sum_i E_i^c \left( 1 - \text{Tr} [\phi_i^\dagger \phi_i] \right) \\
- \sum_{i, a b} \left( [\lambda_i]_{a b} + [\lambda_i^\dagger]_{a b} \right) [n_i^0]_{a b} + \sum_{a, \alpha} \sum_{\mathcal{R}} (D_{\mathcal{R} a})_{\alpha a} + \text{c.c.} \right) \sqrt{[n_i^0]_{a b} (1 - [n_i^0]_{a b})} + \mu N, 
\]

where \(\hat{H}_G^{\text{pp}}(\mathcal{R}, \mathcal{R}^\dagger; \lambda + \eta; \mu) \equiv \sum_{k, \mathcal{R}} \sum_{i, j} \sum_{\alpha, \beta} \mathcal{R}_{\mathcal{R} i a} \epsilon_{k, i j} \mathcal{R}_{\mathcal{R} j b} \hat{f}_{i a}^\dagger \hat{f}_{j b} \\
+ \sum_{\mathcal{R}, i a b} [\lambda_i]_{a b} \hat{f}_{i a}^\dagger \hat{f}_{i b} + \sum_{\mathcal{R}, i a b} [\eta_i]_{a b} \hat{f}_{i a} \hat{f}_{i b} \\
- \sum_{\mathcal{R}, i a} \mu \hat{f}_{i a} \hat{f}_{i a} 
\]
is the GA quasi-particle Hamiltonian of the system, the matrices \(F_{i a}\) and \(\hat{H}_G^{\text{loc}}\) represent the local operators \(\hat{f}_{i a}\) and \(\hat{H}_G^{\text{loc}}\) in a given (arbitrary) basis-set of local multipoles (\(\Gamma, \mathcal{R}\)).

\[
[F_{i a}]_{\Gamma', \Gamma} \equiv \langle \Gamma, \mathcal{R} | \hat{f}_{i a} | \Gamma' \rangle \tag{8}
\]
\[
[\hat{H}_G^{\text{loc}}]_{\Gamma', \Gamma} \equiv \langle \Gamma, \mathcal{R} | \hat{H}_G^{\text{loc}}(\{c_{i a}\}, \{\bar{c}_{i a}\}) | \Gamma' \rangle \tag{9}
\]
|\(\Psi_0\)| is a Slater determinant, \(\mathcal{R}_i, D_i, \lambda_i, \bar{\lambda}_i, \eta_i\) are matrices whose dimension \(\nu_i\) is the number of \(i\) spin-orbitals, \(\phi_i\) are \(2\nu_i\)-dimensional matrices, \(N\) is the total number of electrons (normalized to the number of \(k\)-points \(N\)), and \(\hat{f}_{i a}\) are the so-called “natural” ladder operator, which are related with the “original” ladder operator \(\hat{c}_{i a}\) — i.e., the operators in which the Hubbard model [Eq. (1)] is expressed — by a proper unitary transformation, see the Appendix A.

It is important to observe that only the natural-basis operators \(\hat{f}_{i a}\) are involved in Eq. (6), and not the “original” operators \(\hat{c}_{i a}\). This is because the unitary transformation that relates the original basis and the natural basis has been “gauged away” from the formalism so that it is not necessary to know it explicitly.

For later convenience we observe that the terms involving |\(\Psi_0\)| in Eq. (6) can be substituted with the ground-state energy of \(\hat{H}_G^{\text{pp}}\), which can be written as

\[
\frac{T}{N} \sum_{k, \omega} \text{Tr} \log \left( \frac{1}{i \omega - \mathcal{R} \epsilon_k \mathcal{R}^\dagger - \lambda - \eta + \mu} \right) e^{i \omega \partial^+} \\
= \frac{T}{N} \sum_{k, \omega} \text{Tr} \log \left( \frac{1}{\mathcal{R} \epsilon_k + \mu - \Sigma(i \omega)} \right) e^{i \omega \partial^+} \\
= \frac{T}{N} \sum_{k, \omega} \text{Tr} \log \left( \frac{1}{i \omega - \epsilon_k + \mu - \Sigma(i \omega)} \right) e^{i \omega \partial^+}, \tag{10}
\]

where \(i \omega\) are Fermionic Matsubara frequencies, \(\Sigma(i \omega)\) is given by Eq. (4), \(\mu\) is the chemical potential, and \(\mathcal{R}, \lambda\) and \(\eta\) are block-matrices, whose blocks are \(\mathcal{R}_i, \lambda_i\) and \(\eta_i\), respectively. Note that the renormalization factors in the quasi-particle Green’s function give only a frequency-independent term, that does not contribute because of the Matsubara summation.

We observe that, since we are working at zero temperature, the summation over the Fermionic Matsubara frequencies of Eq. (10) is continuous. On the other hand, according to the slave-bosons theory discretizing the Matsubara summation by assuming that \(\omega = (2m+1)\pi T\) (with \(m\) integer) actually amounts to perform calculations at the finite temperature \(T\). Note that within the finite-temperature Gutzwiller approximation it is possible to make a more accurate estimation of the entropy, which requires to take into account an additional contribution proportional to the temperature. Since in this work we apply GA at zero temperature we do not need to take into account this additional term.

**Gutzwiller expectation values**

Once the GA solution is determined by imposing the saddle point conditions of \(\mathcal{L}_N\) with respect to all of its arguments, the expectation value of any observable can be readily computed. In particular, see the Appendix, it can be proven that the expectation value of any local operator within the site \((\mathcal{R}, i)\) is given by

\[
\langle \Psi_G | \hat{A}_{\mathcal{R} i} (\{\bar{c}_{i a}\}, \{\bar{c}_{i a}\}) | \Psi_G \rangle = \text{Tr} [\phi_i \phi_i^\dagger A_i], \tag{11}
\]

where \(A_i\) is the representation of \(\hat{A}_{\mathcal{R} i}\) in the same basis used in Eqs. (8) and (9).

\[
[A_i]_{\Gamma', \Gamma} \equiv \langle \Gamma, \mathcal{R} | \hat{A}_{\mathcal{R} i} (\{\bar{c}_{i a}\}, \{\bar{c}_{i a}\}) | \Gamma' \rangle. \tag{12}
\]

The average of any inter-site density-matrix operator reduces to calculate

\[
\langle \Psi_G | \hat{c}_{R i a} \hat{c}_{R' j b}^\dagger | \Psi_G \rangle = \sum_{a b} \langle \Psi_0 | (D_{\mathcal{R} a})_{\alpha a} \hat{f}_{R i a} \left( [R_{R i}]_{\alpha, \beta} \hat{f}_{R' j b}^\dagger \right) | \Psi_0 \rangle. \tag{13}
\]

In other words, the inter-site single-particle density matrix averaged on |\(\Psi_G\)| is computed by averaging over |\(\Psi_0\)|.
a renormalized density matrix with “natural” Fermionic operators, which are obtained by replacing the physical ones according to the rule

\[ \hat{c}_{Ria}^\dagger \rightarrow \sum_a [\mathcal{R}_{1a}]_{aa} \hat{f}_{Ria}^a. \] (14)

B. Physical interpretation of the parameters \( \phi_i \) based on the Schmidt decomposition

Let us consider the impurity local many-body space \( \mathcal{V}_i \) generated by the multiplets

\[ |\Gamma, i\rangle = \left[ \hat{c}_{i1}^\dagger \right]^{n_1} \cdots \left[ \hat{c}_{iM}^\dagger \right]^{n_M} |0\rangle, \] (15)

and assume that the same basis has been used in Eqs. (8) and (9).

We define a copy of \( \mathcal{W}_i \) of \( \mathcal{V}_i \) generated by another set of Fock states \( |n, i\rangle \) represented as

\[ |n, i\rangle = \left[ \hat{f}_{i1}^\dagger \right]^{n_1} \cdots \left[ \hat{f}_{iM}^\dagger \right]^{n_M} |0\rangle, \] (16)

where the \( f \) ladder operators anticommute with the \( c \) ladder operators.

Let us now consider a generic pure state within the tensor-product space \( \mathcal{E}_i \equiv \mathcal{V}_i \otimes \mathcal{W}_i \), and represent it as

\[ |\Phi_i\rangle \equiv \sum_{\Gamma_n} |\phi_i\rangle_{\Gamma_n} |\Gamma, i\rangle U_{PH}|n, i\rangle, \] (17)

where \( U_{PH} \) is the particle-hole transformation on the \( f \) degrees of freedom. It can be readily verified that, for any operator \( A \) acting within the space generated by the states \( |\Gamma, i\rangle \),

\[ \langle \Phi_i | \hat{A} |\{\hat{c}_{i\alpha}^\dagger\}, \{\hat{c}_{i\alpha}\} \rangle_{\Gamma, i} = \text{Tr} \{\phi_i \phi_i^\dagger A \}, \] (18)

where \( \phi_i \) is the matrix of coefficients in Eq. (17), and

\[ [A]_{\Gamma \Gamma'} \equiv \langle \Gamma, i | \hat{A} |\{\hat{c}_{i\alpha}^\dagger\}, \{\hat{c}_{i\alpha}\} \rangle |\Gamma', i\rangle. \] (19)

Furthermore, it can be shown that

\[ \langle \Phi_i | \hat{c}_{i\alpha}^\dagger \hat{f}_{ia} |\Phi_i\rangle = \text{Tr} \phi_i^a F_{ia}^\dagger F_{ia} \] (20)
\[ \langle \Phi_i | \hat{f}_{ab} \hat{f}_{ia} |\Phi_i\rangle = \text{Tr} \phi_i^a \phi_i^b F_{ia}^\dagger F_{ia} \] (21)
\[ \langle \Phi_i | \phi_i \phi_i^\dagger \rangle = \text{Tr} \phi_i^a \phi_i^a. \] (22)

Note that in order to prove Eqs. (20) and (21) we need to remember that we have expanded \( |\Phi_i\rangle \) in Fock states and that the matrix elements of the ladder operators are real in this basis.

Thanks to Eqs. (18)-(22) the GA Lagrange function, see Eq. (6), can be rewritten as follows

\[ \mathcal{L}_N[\Phi, 3\lambda; \mathcal{R}, \mathcal{R}^\dagger, \lambda, \eta, \mu; \mathcal{D}, \mathcal{D}^\dagger, \lambda^c; n^0] = \frac{T}{N} \sum_{k,\omega} \text{Tr} \log \left( \frac{i \omega - \mathcal{R}_{kk} \mathcal{R}_{kk}^\dagger - \lambda - \eta + \mu}{1 - \lambda + \mu} \right) e^{i \omega 0^+} + \sum_i \left[ \langle \Phi_i | \mathcal{H}^{\text{emb}}[\mathcal{D}_i, \mathcal{D}_i^\dagger; \lambda^c] |\Phi_i\rangle + E_i^c (1 - \langle \Phi_i | \Phi_i\rangle) \right] - \sum_i \left[ \sum_{\alpha} \left[ |\lambda_{\alpha}|_0 + |\lambda^c_{\alpha}|_0 \right] n^0_{\alpha} + \sum_{\alpha \beta} \left[ (|\lambda_{\alpha}|_0 - |\lambda^c_{\alpha}|_0) \sqrt{|n^0_{\alpha}|_0 (1 - |n^0_{\alpha}|_0)} \right] + \mu N, \right] \] (23)

where

\[ \mathcal{H}^{\text{emb}}[\mathcal{D}_i, \mathcal{D}_i^\dagger; \lambda^c] \equiv \mathcal{H}^{\text{loc}}[\{\hat{c}_{i\alpha}^\dagger\}, \{\hat{c}_{i\alpha}\}] + \sum_{\alpha \beta} \left[ |\mathcal{D}_{i\alpha}|_0 \hat{c}_{i\alpha}^\dagger \hat{f}_{ia} + \text{H.c.} \right] + \sum_{\alpha \beta} |\lambda_{\alpha}|_0 \hat{f}_{ib} \hat{f}_{ia} \] (24)

and we made use of Eq. (10).

Since the GA solution is stationary with respect to \( |\Phi_i\rangle \) and \( E_i^c \), \( \mathcal{H}^{\text{emb}} \) can be interpreted as an impurity Hamiltonian whose bath has the same dimension of the impurity, and that is determined by the GA procedure in order to describe the entanglement between the impurity and the rest of the system.

We point out that, in principle, a Hamiltonian whose bath has the same dimension of the impurity is sufficient to represent exactly the ground-state local properties of the Hubbard model, as it can be readily shown making use of the Schmidt decomposition. Here we have shown that the GA consists in assuming that the form of this Hamiltonian is limited to an Anderson impurity model, see Eq. (24), where the coefficients \( \mathcal{D}_i, \lambda^c_\alpha \) are determined from the stationarity of the Lagrange function [Eq. (23)]. This insight makes it clear that taking into account all of the components of \( \phi_i \) is crucial to describe accurately the local physics of the system — including
the off-diagonal matrix elements in a basis that diagonalizes $H^{\text{loc}}$.

**Implementation of the symmetries**

It is useful to understand how to translate in terms of the states $|\Phi_i\rangle$, see Eq. (17), symmetry conditions and variational assumptions initially defined in terms of the matrices $\phi_i$.

As an example, here we show how to impose the possible variational assumption that the matrix $\phi_i$ — that is connected to the reduced density matrix to the $(R, i)$ site through Eq. (11) — couples only local multiplets with the same number of electrons. According to Eq. (17), this condition implies that $|\Phi_i\rangle$ is a linear combination of product-states where

$$N_G = N_{\text{full}} - N_n,$$  \hspace{1cm} (25)

where $N_{\text{full}}$ is the maximum number of electrons allowed in the many-body local space generated by the $f_{ia}^\dagger$ ladder operators (e.g., $N_{\text{full}} = 2$ for the single-band Hubbard model). In conclusion, from the argument above we deduce that

$$\hat{N}^\text{tot}_i |\Phi_i\rangle = \hat{N}^\text{full}_i |\Phi_i\rangle,$$  \hspace{1cm} (26)

where

$$\hat{N}^\text{tot}_i \equiv \sum_a f_{ia}^\dagger f_{ia} + \sum_a \hat{c}_{ia}^\dagger \hat{c}_{ia}$$  \hspace{1cm} (27)

is the total number operator in the embedding system, and $N^\text{full}_i$ is the number of orbitals (including the spin) in the $R, i$ space. Of course, the variational assumption [Eq. (28)] reduces considerably the computational complexity of the problem.

A more complete discussion on how to implement the symmetries within the picture derived above will be given in a separate publication.

**C. Numerical solution of the GA Lagrange equations**

It can be readily shown that the saddle-point condition of $L_N$ with respect to all of its arguments provides the following system of Lagrange equations:

$$\frac{1}{N} \left[ \sum_k \Pi_i f(R \epsilon_k R^\dagger + \lambda + \eta - \mu) \Pi_i \right]_{ab} = 0 \quad \forall a \neq b$$  \hspace{1cm} (28)

$$\frac{1}{N} \left[ \sum_{ia} \Pi_i f(R \epsilon_k R^\dagger + \lambda + \eta - \mu) \Pi_i \right]_{aa} = N$$  \hspace{1cm} (29)

$$\frac{1}{N} \left[ \sum_k \Pi_i f(R \epsilon_k R^\dagger + \lambda + \eta - \mu) \Pi_i \right]_{ba} = [n^0_i]_{ab}$$  \hspace{1cm} (30)

as follows

$$\frac{1}{N} \left[ \sum_k \Pi_i f(R \epsilon_k R^\dagger + \lambda + \eta - \mu) \Pi_i \right]_{ba} = \left\{ \begin{array}{l} \frac{1}{2} + T \sum_n G^{qp}_i(z_n) \end{array} \right\}_{ba}$$  \hspace{1cm} (38)

$$\frac{1}{N} \left[ \frac{1}{R_i} \sum_k \Pi_i f(R \epsilon_k R^\dagger + \lambda + \eta - \mu) \Pi_i \right]_{aa} = \left\{ \begin{array}{l} \frac{1}{R_i} T \sum_n (z_n - \lambda_i - \eta_i + \mu) G^{qp}_i(z_n) - \Pi_i \end{array} \right\}_{aa}.$$  \hspace{1cm} (39)
We observe that $G_{i}^{op}$ can be rewritten as

$$G_{i}^{op}(z) = \frac{1}{R_{i}} \Pi \frac{1}{N} \sum_{k} \frac{1}{z - \epsilon_{k} + \mu - \Sigma(z)} \Pi \frac{1}{R_{i}}$$

$$\equiv \frac{1}{R_{i}} G_{i}(z) \frac{1}{R_{i}}$$

(40)

where $\Sigma(z)$, which represents the GA approximation for the self-energy, is a block-matrix, whose blocks are given by

$$\Sigma_{i}(z) \equiv -\frac{1}{k} \frac{I - R_{i} R_{i}^{\dagger}}{R_{i} R_{i}^{\dagger}} \frac{1}{\lambda_{i} + \eta} \frac{1}{R_{i}}$$

$$- \mu \frac{I - R_{i} R_{i}^{\dagger}}{R_{i} R_{i}^{\dagger}} ,$$

(41)

and

$$G_{i}(z) \equiv \Pi \frac{1}{N} \sum_{k} \frac{1}{z - \epsilon_{k} + \mu - \Sigma(z)} \Pi .$$

(42)

is the GA approximation for the coherent part of the local Green’s function.

We point out that our definition of the Gutzwiller self-energy includes both the on-site one-body part of $H$ and the chemical potential.

Within the above definitions, it can be readily shown that Eqs. (38) and (39) can be represented also as

$$\frac{1}{N} \left[ \sum_{k} \Pi \frac{1}{N} f(R_{i} \epsilon_{k} R_{i}^{\dagger} + \lambda + \eta - \mu) \Pi \right]_{ba} =$$

$$\frac{1}{2} \frac{1}{R_{i}} \left[ \sum_{n} G_{i}(z_{n}) \frac{1}{R_{i}} \right]_{ba}$$

(43)

$$\frac{1}{N} \left[ \frac{1}{R_{i}} \sum_{k} \Pi \frac{1}{N} f(R_{i} \epsilon_{k} R_{i}^{\dagger} + \lambda + \eta - \mu) \Pi \right]_{oa} =$$

$$\frac{1}{2} \frac{1}{R_{i}} \left[ \sum_{n} \left[ (z_{n} + \mu - \Sigma(z_{n})) G_{i}(z_{n}) - \Pi \right] \frac{1}{R_{i}} \right]_{oa} .$$

(44)

Note that the evaluation of Eqs. (43) and (44) requires only to know the local Green’s functions $G_{i}$ of the correlated sites, see Eq. (12). As we are going to show, the operation to compute $G_{i}$ at given $\Sigma$, relates with the embedding procedure of DMCFT.

We observe that the computational-time necessary to calculate Eq. (42) scales as the square of the number of correlated atoms. On the contrary, Eqs. (28)–(31) require to diagonalize $\epsilon_{k}$, whose computational-time scales as the cube the number of total atoms (correlated and not). Consequently, Eqs. (34) and (35) can be preferable if the unit cell of contains many atoms and/or if only few orbitals are correlated.

The algorithm

A possible way to compute the Gutzwiller solution is the following. (i) Given $(R, \lambda)$, we use Eqs. (28)–(29) to compute the Lagrange multipliers $\mu$ and $\eta$ and the corresponding $(\psi_{e})$, which determines $n_{e}^{\dagger}$ through Eq. (30), $D_{i}$ through Eq. (31), and $\lambda_{i}^{\dagger}$ through Eq. (33). (ii) Thereafter, we solve the embedding Hamiltonians, see Eq. (33), to compute $(\Phi_{i})$, which determine the left members of Eqs. (34) and (35). The equations (34) and (35) are verified if and only if $(R, \lambda)$ is the correct set of variational parameters.

In conclusion, the solution of the Gutzwiller equations can be formulated as a root problem for $(R, \lambda)$, which can be formally written as

$$(F^{(1)}_{i} [R, \lambda], F^{(2)}_{i} [R, \lambda]) = 0 \ \forall i .$$

Note that the vector-functions $F_{i}$, see Eqs. (34) and (35), can be evaluated independently through the numerical steps outlined above.

D. Summary main results of Sec. II

In this section we have expressed the GA Lagrange function derived in Refs. 28–30 see Eq. (6), in the convenient form [Eq. (23)], from which follows an exceptionally efficient numerical scheme, see Eqs. (28)–(35) and text below.

We have shown that our algorithm consists in solving iteratively a series of Anderson impurity Hamiltonians whose bath has the same dimension as the impurity, see Eq. (24). This finding enables for a useful interpretation of the Gutzwiller variational parameters based on the Schmidt decomposition, which enables us to solve Eq. (24) using the Lanczos method, and opens up the possibility to exploit techniques such as those developed in quantum-chemistry in order to further speed-up our algorithm.

We have observed that alternative expressions for the GA Lagrange equations (28)–(31) can be derived using the Green’s function formalism, see Eqs. (43) and (44). These expressions can be preferable if the unit cell of the system contains many atoms and/or if only few orbitals are correlated.

We point out that in our numerical scheme the treatment of the correlation effects scales linearly with the number of correlated atoms per unit cell (as in LDA+DMFT). Since linear-scaling DFT methods are also available68 the linear-scaling property of our solver opens up the possibility to study correlated systems with extremely large supercells, even containing several hundreds of correlated atoms.

In Sec. B of the appendix the numerical strategy discussed in this section is generalized to Anderson impurity models.
III. THE GUTZWILLER-BAYM-KADANOFF FUNCTIONAL

In this section we formulate the GA of the Hubbard model, see Eq. (1), as the saddle-point of a functional of the coherent part of the local Green’s function, and we show that the mathematical structure of this functional resembles the BK theory on top of the DMFT approximation.

Let us rewrite Eq. (23) as follows,

\[
\mathcal{L}^\prime[\Phi, E^c; \mathcal{R}, \mathcal{R}^\dagger, \lambda, \eta, \mu; \mathcal{D}, \mathcal{D}^\dagger, \lambda^c; n^0] = \\
\frac{T}{N} \sum_{k, \omega} \text{Tr} \log \left( \frac{1}{i\omega - \epsilon_k + \mu - \Sigma(i\omega)} \right) + \mu N + \\
\sum_i \Theta_{\hat{H}_{\text{loc}}}^{\text{loc}}[\Phi_i, E^c_i; \mathcal{R}_i, \mathcal{R}_i^\dagger, \lambda_i; \mathcal{D}_i, \mathcal{D}_i^\dagger, \lambda_i^c; n_i^0],
\]

where we have implicitly assumed that the regularization factor \( e^{\text{loc}} \) is present in the Matsubara summation,

\[
\Theta_{\hat{H}_{\text{loc}}}^{\text{loc}}[\Phi_i, E^c_i; \mathcal{R}_i, \mathcal{R}_i^\dagger, \lambda_i; \mathcal{D}_i, \mathcal{D}_i^\dagger, \lambda_i^c; n_i^0] \equiv \\
(\Phi_i | \hat{H}_{\text{loc}}^{\text{ab}} | \mathcal{D}_i, \mathcal{D}_i^\dagger, \lambda_i^c | \Phi_i) + E^c_i (1 - (\Phi_i | \Phi_i)) - \\
\sum_{ab} ((\lambda_a)^{\text{loc}} + (\lambda^c_a)^{\text{loc}}) \langle n_i^0 \rangle_{ab} - \\
\sum_{a\alpha} (\mathcal{D}_{i\alpha a} | \mathcal{R}_i)_{a\alpha} + \text{c.c.} \sqrt{\langle n_i^{\text{loc}} \rangle_{aa} (1 - \langle n_i^{\text{loc}} \rangle_{aa})},
\]

and \( \Theta_{\hat{H}_{\text{loc}}}^{\text{loc}} \) depends on \( \hat{H}_{\text{loc}}^{\text{loc}} \) through Eq. (24). Note that, thanks to the formal manipulations of Eq. (10), the quasiparticle parameters \( \mathcal{R}, \lambda, \eta \) affect the first term of \( \mathcal{L}^\prime \) only through the Gutzwiller self-energy \( \Sigma \), which was defined in Eq. (11).

It is useful to promote the self-energy to an independent variable by introducing the following additional Lagrange-Legendre term in Eq. (46),

\[
\sum_i \frac{T}{N} \sum_{\omega} \sum_{ab} (-\mathcal{G}_i(i\omega)_{ab} \Sigma(i\omega)) \\
\left( -i\omega \frac{1 - R_i}{R_i R_i^\dagger} + \frac{1}{R_i} (\lambda + \eta_k) \frac{1}{R_i^\dagger} + \\
-\mu \frac{1 - R_i}{R_i R_i^\dagger} \right) \bigg|_{ab},
\]

where \( \mathcal{G}_i(i\omega) \) are, at the present stage, the Lagrange multipliers used to enforce the GA definition of \( \Sigma(i\omega) \), see Eq. (11). Nevertheless, we observe that by deriving the so obtained Lagrange-function with respect to \( \Sigma(i\omega) \) one obtain the Dyson equation for the \( i \) local Green’s function,

\[
\mathcal{G}_i(i\omega) = \Pi_i \left( \frac{1}{N} \sum_k \frac{1}{i\omega - \epsilon_k + \mu - \Sigma(i\omega)} \right) \Pi_i,
\]

where \( \Pi_i \) is the projector onto the \( i \) local subspace.

The above formal manipulations enable us to express the GA in terms of the following Lagrange-function

\[
\mathcal{L}^\prime \left[ \mathcal{G}, \Sigma; \Phi, E^c; \mathcal{R}, \mathcal{R}^\dagger, \lambda, \eta, \mu; \mathcal{D}, \mathcal{D}^\dagger, \lambda^c; n^0 \right] \equiv \\
\frac{T}{N} \sum_{k, \omega} \text{Tr} \log \left( \frac{1}{i\omega - \epsilon_k + \mu - \Sigma(i\omega)} \right) - \\
\sum_i \sum_{\omega} \text{Tr} \left[ \Sigma_i(i\omega) \mathcal{G}_i(i\omega) \right] + \\
\sum_i \mathcal{G}_{\text{loc}}^i \left[ \mathcal{G}_i, \mu; \Phi_i, E^c_i, \mathcal{R}_i, \mathcal{R}_i^\dagger, \lambda_i, \eta_i; \mathcal{D}_i, \mathcal{D}_i^\dagger, \lambda_i^c; n_i^0 \right] = \\
\frac{T}{N} \sum_{k, \omega} \text{Tr} \log \left( \frac{1}{i\omega - \epsilon_k + \mu - \Sigma(i\omega)} \right) + \\
\sum_i \sum_{\omega} \text{Tr} \left[ \Sigma_i(i\omega) \mathcal{G}_i(i\omega) \right] + \\
\sum_i \mathcal{G}_{\text{loc}}^i \left[ \mathcal{G}_i, \mu; \Phi_i, E^c_i, \mathcal{R}_i, \mathcal{R}_i^\dagger, \lambda_i, \eta_i; \mathcal{D}_i, \mathcal{D}_i^\dagger, \lambda_i^c; n_i^0 \right] ,
\]

where

\begin{align*}
\mathcal{G}_{\text{loc}}^i &\equiv \mathcal{G}_{\text{loc}}^i \left[ \mathcal{G}_i, \mu; X_i(\mathcal{G}_i, \mu) \right] ,
\end{align*}

which can be substituted back in Eq. (50).

In conclusion, we have demonstrated that the GA solution is the saddle-point with respect to \( \mathcal{G} \) and \( \Sigma \) of the functional

\[
\Omega^{\text{GA}}[\mathcal{G}, \Sigma, \mu] \equiv \frac{T}{N} \sum_{k, \omega} \text{Tr} \log \left( \frac{1}{i\omega - \epsilon_k + \mu - \Sigma(i\omega)} \right) + \\
\sum_i \mathcal{G}_{\text{loc}}^i \left[ \mathcal{G}_i, \mu; X_i(\mathcal{G}_i, \mu) \right] ,
\]

which resembles the BK theory on top of the DMFT approximation.

We point out that, remarkably, the functional \( \mathcal{G}_{\text{loc}}^{\text{GA}} \) depends on the non-local dispersion \( \epsilon_k \) only through the coherent part of the local Green’s functions \( \mathcal{G}_i \). In other words, it is determined only by \( \hat{H}_{\text{loc}}^{\text{loc}} \) and \( \mathcal{N} \), and is formally analogous to \( \Phi_{\text{loc}}^i \) and \( \sum_{\omega} \text{Tr}[\mathcal{G}_i^c(i\omega)] + \mu N \), where \( \Phi_{\text{loc}}^i \) is the impurity Luttinger functional corresponding to the \( i \) on-site interaction, and \( \sum_{\omega} \text{Tr}[\mathcal{G}_i^c(i\omega)] \) is the additional term arising from having included the on-site interaction.
quadartic part $c_{\text{loc}}$ of the Hamiltonian and the chemical potential $\mu$ within the definition of the self-energy. Note that, since the on-site quadratic operators have to be treated together with the interaction within the GA, the Gutzwiller approximation for $\Phi^{L}_{\text{DMFT}}$ alone can not be defined in general.

A. Summary main results of Sec. III

In this section we have derived a functional formulation of the GA which has essentially the same formal structure of the Baym-Kadanoff theory on top of the DMFT approximation, see Eq. (53), made exception for the following technical differences. (I) The Gutzwiller-Baym-Kadanoff functional depends only on the coherent part of the Green's function, see Eq. (10) - (12). (II) Within the GA it is necessary to treat the quadratic part of the local Hamiltonian together with the interaction, see Eq. (2) and text below Eq. (53). This result clarifies the connection between the GA and DMFT.

IV. FUNCTIONAL FORMULATION OF LDA+GA

Approximations to DFT represent the state of the art of materials simulations. DFT calculations based on the local density approximation (LDA) enable to attack theoretically a wide class of materials, but are generally not satisfactory for the so-called “strongly-correlated” systems, such as, e.g., the high-$T_{c}$ superconductors, the transition metal oxides and the rare-earth compounds. In order to study this important class of materials, several “hybrid” techniques, such as LDA+U, LDA+DMFT and LDA+GA have been developed.

In this section we discuss our implementation of the LDA+GA method.

A. The correlated orbitals

The application of any LDA+X method requires the identification of a proper subset of “correlated” orbitals (e.g., $d$ or $f$), that we represent with the symbol $P$.

The correlated orbitals are determined on a physical basis. Usually, they are constructed using Wannier function methods, e.g., maximally localized Wannier functions or quasi-atomic minimal basis set orbitals. In particular, in this work, we refer to the construction of Haule et al., see Ref. [13] which is exploited in our numerical implementation.

Given a set of $P$-orbitals, we introduce an orthonormal subset of “uncorrelated” orbitals $Q$ spanning the orthogonal complement to the corresponding $P$ linear-space.

For later convenience, we expand the field-operator as

$$\hat{\Xi}(\mathbf{r}, \sigma) = \sum_{\sigma'} \sum_{k_i \pi \in P} \xi_{k_i \sigma}(\mathbf{r}) \chi_{\sigma'}(\mathbf{r}) \hat{c}_{k_{i \pi} \sigma} + \hat{\Xi}_Q(\mathbf{r}, \sigma)$$

$$\equiv \sum_{\mathbf{r}} \hat{\Xi}_{P_i}(\mathbf{r}, \sigma) + \hat{\Xi}_Q(\mathbf{r}, \sigma), \quad (54)$$

where we have chosen a single-particle basis-set with factorized spin and orbital degrees of freedom, and $\hat{\Xi}_Q$ is the component of the field-operator that corresponds to the $Q$ orbitals. Equation (54) provides a prescription to express any one-body operator $A$ in second quantization as

$$\hat{A} = \sum_{\sigma} \int d\mathbf{r} \hat{\Xi}(\mathbf{r}, \sigma) A \hat{\Xi}(\mathbf{r}, \sigma) \equiv \sum_{\mathbf{r}} \hat{A}_{i}^{\text{loc}} + \hat{A}_{i}^{\text{bop}}, \quad (55)$$

where

$$\hat{A}_{i}^{\text{loc}} \equiv \sum_{\sigma} \int d\mathbf{r} \hat{\Xi}_{P_i}(\mathbf{r}, \sigma) A \hat{\Xi}_{P_i}(\mathbf{r}, \sigma) \quad (56)$$

$$\hat{A}_{i}^{\text{bop}} \equiv \hat{A} - \sum_{\mathbf{r}} \hat{A}_{i}^{\text{loc}}. \quad (57)$$

B. Functional formulation of LDA+GA

The purpose of this section is to derive a functional formulation of the LDA+GA method with the same mathematical structure of LDA+DMFT.

1. The LDA+DMFT functional

The solution of the LDA+DMFT method is the saddle point of the following functional

$$\Omega_N[\rho(\mathbf{r}), J(\mathbf{r}); G_{i}^{\text{loc}}(i\omega), \Sigma_{i}^{\text{loc}}(i\omega); \mu] =$$

$$\frac{T}{N} \sum_{\omega} \text{Tr} \log \left( i\omega + \Delta - J + \mu - \Sigma_{i}^{\text{loc}}(i\omega) \right)$$

$$- \sum_{\omega} \sum_{i} T \text{Tr} \left[ \Sigma_{i}^{\text{loc}}(i\omega) G_{i}^{\text{loc}}(i\omega) \right]$$

$$+ \sum_{i} \left[ \Phi_{i}^{L}[G_{i}^{\text{loc}}] - \Phi_{i}^{f}[G_{i}^{\text{loc}}] \right] + \mu N$$

$$+ E_{\text{exc}}^{\text{LDA}}[\rho] + E_{\text{ion}}[\rho] + E_{\text{ion-ion}} - \int d\mathbf{r} J(\mathbf{r}) \rho(\mathbf{r}). \quad (58)$$

where $\mu$ is the chemical potential, $\rho(\mathbf{r})$ is the electron-density, $J(\mathbf{r})$ is the corresponding constraining-field and $\hat{J} \equiv \sum_{\sigma} \int d\mathbf{r} \hat{\Xi}(\mathbf{r}, \sigma) J(\mathbf{r}) \hat{\Xi}(\mathbf{r}, \sigma) \quad (59)$

is the corresponding operator. The functional $\Phi_{i}^{L}$ is the $i$-impurity Luttinger functional, and $\Phi_{i}^{f}$ is a proper double-counting correction.
The total number of electrons $N$ (correlated and uncorrelated) is pre-determined by the charge-neutrality condition of the system.

For simplicity, in the rest of this sub-section we will assume a linear double-counting functional, represented as

$$\Phi_{V^{dc}}[G^\text{loc}_i] = V^{dc}_i T \sum_\omega \text{Tr} \left[ G^\text{loc}_i (i\omega) \hat{N}^\text{loc}_i \right]$$

$$\equiv V^{dc}_i N^\text{loc}_i ,$$

(60)

where $\hat{N}^\text{loc}_i$ is the number operator for the correlated electrons at the site $i$, and $V^{dc}_i$ is a given real number. The generalization to the problem of non-linear double counting functionals will be obtained in Sec. IV D by reducing it to the simpler case of linear double-counting.

Note that, under the assumption [Eq. (60)], the LDA+DMFT functional can be written as

$$\Omega_{V^{dc}; N}[\rho, J; G^\text{loc}, \Sigma^\text{loc}; \mu] \equiv \Omega_{V^{dc}; N}^{\text{KSH}}[J; G^\text{loc}, \Sigma^\text{loc}; \mu] - \int dr J(r) \rho(r) + E_{\text{LDA}}[\rho] + E_{\text{ion}}[\rho] + E_{\text{ion-ion}} ,$$

(61)

where

$$\Omega_{V^{dc}; N}^{\text{KSH}}[J; G^\text{loc}, \Sigma^\text{loc}; \mu] =$$

$${T \over N} \sum_\omega \text{Tr} \log \left( \frac{1}{i\omega + \mathcal{R} \delta_{\text{hop}} - \hat{N}^\text{hop} \mathcal{R}^\dagger - \lambda - \eta + \mu} \right) +$$

$$\sum_i \left[ \langle \Phi_i \rangle - \Delta^\text{loc} \{ \hat{c}_{i\alpha} \dagger, \{ \hat{c}_{i\alpha} \} \} + J^\text{loc}_{\text{int}} \{ \{ \hat{c}_{i\alpha} \dagger, \{ \hat{c}_{i\alpha} \} \} \right] + \hat{H}^\text{int}_{\text{loc}}[\{ \hat{c}_{i\alpha} \dagger, \{ \hat{c}_{i\alpha} \} \} - V^{dc}_i \sum_\alpha \hat{c}_{i\alpha} \dagger \hat{c}_{i\alpha} +$$

$$\sum_{aa} \left( [\mathcal{D}]_{aa} \hat{c}_{i\alpha} \dagger \hat{c}_{i\alpha} + \text{H.c.} \right) + \sum_{ab} [\lambda^\text{loc}_{iab}] + \sum_{iab} \left( [\mathcal{D}]_{iab} [\mathcal{R}]_{iab} + \text{c.c.} \right) \sqrt{\langle n^0_{iab} \rangle (1 - \langle n^0_{iab} \rangle )} + \mu N ,$$

(64)

see Eqs. (56) and (57).

Note that $\mathcal{R}$ is, by definition, a block matrix acting as the identity within the uncorrelated space $Q$, and with blocks $\mathcal{R}_i$ within the corresponding $i$ correlated spaces. The matrices $\lambda$ and $\eta$ are instead zero within the $Q$ space, and with blocks $\lambda_i$ and $\eta_i$, respectively, within the corresponding $i$ correlated spaces.

As in LDA+DMFT, The total number of electrons $N$ (correlated and uncorrelated) is pre-determined by the charge-neutrality condition of the system.

$$\frac{T}{N} \sum_\omega \text{Tr} \log \left( \frac{1}{i\omega + \Delta - J + \mu - \Sigma^\text{loc}(i\omega)} \right) - \sum_i \sum_\omega \text{Tr} \left[ \Sigma^\text{loc}_i (i\omega) G^\text{loc}_i (i\omega) \right] + \sum_i \left[ \Phi_i [G^\text{loc}_i] - \Phi_{V^{dc}} [G^\text{loc}_i] \right] + \mu N$$

is the DMFT approximation to the BK functional for the Kohn-Sham-Hubbard (KSH) Hamiltonian

$$\hat{H}_{V^{dc}}^{\text{KSH}}[J] \equiv -\Delta + \sum_\sigma \int dr \hat{\Xi}^\dagger (r, \sigma) J(r) \hat{\Xi} (r, \sigma) + \sum_i \hat{H}^\text{int}_i - \sum_i V^{dc}_i \hat{N}^\text{loc}_i .$$

(63)

2. The LDA+GA functional

The LDA+GA functional is obtained by substituting the DMFT functional [Eq. (62)] of $\hat{H}_{V^{dc}}^{\text{KSH}}[J]$, see Eq. (63), with the corresponding GA functional, see Eq. (23). This gives the following expression:

$$\Omega_{V^{dc}; N}^{\text{KSH}}[J; \Phi, E^c, \mathcal{R}, \mathcal{R}^\dagger, \lambda, \eta, \mu, \mathcal{D}, \mathcal{D}^\dagger, \chi^c, n^0] =$$

$$\frac{T}{N} \sum_\omega \text{Tr} \log \left( \frac{1}{i\omega + \mathcal{R} \delta_{\text{hop}} - \hat{N}^\text{hop} \mathcal{R}^\dagger - \lambda - \eta + \mu} \right) +$$

$$\sum_i \left[ \langle \Phi_i \rangle - \Delta^\text{loc} \{ \hat{c}_{i\alpha} \dagger, \{ \hat{c}_{i\alpha} \} \} + J^\text{loc}_{\text{int}} \{ \{ \hat{c}_{i\alpha} \dagger, \{ \hat{c}_{i\alpha} \} \} \right] + \hat{H}^\text{int}_{\text{loc}}[\{ \hat{c}_{i\alpha} \dagger, \{ \hat{c}_{i\alpha} \} \} - V^{dc}_i \sum_\alpha \hat{c}_{i\alpha} \dagger \hat{c}_{i\alpha} +$$

$$\sum_{aa} \left( [\mathcal{D}]_{aa} \hat{c}_{i\alpha} \dagger \hat{c}_{i\alpha} + \text{H.c.} \right) + \sum_{ab} [\lambda^\text{loc}_{iab}] + \sum_{iab} \left( [\mathcal{D}]_{iab} [\mathcal{R}]_{iab} + \text{c.c.} \right) \sqrt{\langle n^0_{iab} \rangle (1 - \langle n^0_{iab} \rangle )} + \mu N ,$$

(64)

C. Charge self-consistency and KSH Hamiltonian

In this section we discuss the general structure of our implementation of the charge self-consistent LDA+GA method.

The stationarity condition of Eq. (64) with respect to $\rho(r)$ gives that

$$J(r) = \frac{\delta E_{\text{LDA}}}{\delta \rho(r)} + \frac{\delta E_{\text{ion}}[\rho]}{\delta \rho(r)} ,$$

(65)

while the stationarity condition with respect to $J(r)$ gives
\[
\rho^{GA}(r) = \frac{1}{N} \sum_{\omega} \text{Tr} \left( \frac{1}{i \omega + \mathcal{R}} \Delta^{\text{hop}} \Delta^{\text{hop} \dagger} \mathcal{R} \right) \\
+ \sum_{i} \sum_{\sigma} \langle \Phi_i | \hat{\Xi}_{pi}^{\dagger} (r, \sigma) \hat{\Xi}_{pi} (r, \sigma) | \Phi_i \rangle \equiv \langle \Psi_G | \sum_{\sigma} \hat{\Xi}_{pi}^{\dagger} (r, \sigma) \hat{\Xi}_{pi} (r, \sigma) | \Psi_G \rangle,
\]

FIG. 1: (Colors online) Schematic flow-chart of the LDA+GA charge self-consistent procedure for linear double-counting. The step concerning the solution of \( \hat{H}_{\text{KSH}} \) is implemented as in Sec. II C, where the GA expectation value of the local part of the density operator is not computed from the quasi-particle Green’s function, but is computed using \( | \Phi_i \rangle \) accordingly to Eqs. (11) and (18). Finally, the stationarity condition with respect to the variables \( | \Phi_i \rangle, E_i^c, R_i, R_i^\dagger, \lambda_i, \eta_i, \mu_i, D_i, D_i^\dagger, \chi_i^c, n_i^0 \) amounts to solve within the GA the KSH Hamiltonian [Eq. (63)] following the procedure described in Sec. II C.

In conclusion, under the assumption [Eq. (63)], both LDA+GA and LDA+DMFT can be solved numerically as follows, see Fig. 1. (I) given an initial electron-density \( \rho_0(r) \) (e.g., the LDA electron-density) we construct \( \hat{H}_{\text{KSH}} \) using Eqs. (65) and (65). (II) we solve \( \hat{H}_{\text{KSH}} \) within the GA, see Sec. II C, and compute the corresponding electron-density \( \rho^{GA}(r) \) according to Eq. (66). The procedure is iterated until the charge self-consistency condition is satisfied.

The generalization of the above numerical procedure to a more general class of double-counting functionals is given in the next section.

D. The LDA+GA for general double-counting

In general, the double-counting functional is not a linear function of the on-site occupations of correlated electrons \( \rho^{\text{loc}}_i \). Let us consider the following generalization of Eq. (64):

\[
V_i^{dc} \langle \Phi_i | \sum_{\alpha} \hat{c}_{i\alpha}^\dagger \hat{c}_{i\alpha} | \Phi_i \rangle \rightarrow E_i^{dc}[\langle \Phi_i | \sum_{\alpha} \hat{c}_{i\alpha}^\dagger \hat{c}_{i\alpha} | \Phi_i \rangle],
\]

where \( E_i^{dc} \) is a generic non-linear function.

In order to solve the LDA+GA equations in this general case it is useful to promote the average local occupations to independent variables by adding the following Lagrange-Legendre term to Eq. (64),

\[
\sum_i V_i^{dc} \left[ \langle \Phi_i | \sum_{\alpha} \hat{c}_{i\alpha}^\dagger \hat{c}_{i\alpha} | \Phi_i \rangle - \rho^{loc}_i \right],
\]

which gives the following expression:

\[
\Omega^{\text{KSH}}_{V_i^{dc}; N_i^{\text{loc}}}[\rho^{\text{loc}}, V_i^{dc}; \rho, J, \Phi, E^c, R, \mathcal{R}^\dagger, \lambda, \eta, \mu, D, D^\dagger, \chi^c, n^{0}] = \Omega^{\text{KSH}}_{V_i^{dc}; N_i^{\text{loc}}}[\rho, J; \Phi, E^c, R, \mathcal{R}^\dagger, \lambda, \eta, \mu, D, D^\dagger, \chi^c, n^{0}] + \sum_i [E_i^{dc}[N_i^{\text{loc}}] - V_i^{dc} N_i^{\text{loc}}],
\]

where \( \Omega^{\text{KSH}}_{V_i^{dc}; N_i^{\text{loc}}} \) is defined in Eq. (64).

Equation (68) enables us to reduce the LDA+GA problem for generic double-counting to the problem solved in Sec. IV C. In fact, in the saddle-point condition with respect to the variables \( \rho(r), J(r), | \Phi_i \rangle, E_i^c, R_i, R_i^\dagger, \lambda_i, \eta_i, \mu, D_i, D_i^\dagger, \chi_i^c, n_i^{0} \) at fixed \( N_i^{\text{loc}} \) and \( V_i^{dc} \) — of the so-modified Eq. (64) can be solved numerically following the procedure of Sec. IV C. see Fig. 1.

The stationarity conditions with respect to \( N_i^{\text{loc}} \) and
FIG. 2: (Colors online) Schematic flow-chart of the LDA+GA outer loop that determines the double-counting potentials $V^{\text{dc}}_i$. The step concerning the solution of the problem at fixed $V^{\text{dc}}_i$ is implemented as in Fig. 1, see Sec. IV C.

We have derived a functional formulation of the LDA+GA method that has the same mathematical structure of LDA+DMFT see Eqs. (64) and (66). This parallelism has enabled us to use the same LAPW interface between DMFT/GA and the LDA code, and suggests possible synergistic combinations between the two methods.

We have derived a very stable and numerically efficient implementation of the LDA+GA method, whose structure is as follows. (I) The double-counting potentials $V^{\text{dc}}_i$ are determined by the outer loop represented in Fig. 2. (II) Each iteration of the outer loop requires to calculate LDA+GA solution at fixed $V^{\text{dc}}_i$ — i.e., the saddle-point of the functional [Eq. (64)], — which is computed numerically using the charge self-consistent procedure represented in Fig. 1. Each iteration of the charge self-consistency loop consists in solving the Kohn-Sham Hubbard Hamiltonian determined by the input electron-density according to Eq. (63) and to compute the corresponding output electron-density according to Eq. (66) until convergence. (III) The Kohn-Sham Hubbard Hamiltonian is solved using the procedure given in Sec. IV C.

V. THE PRESSURE-VOLUME PHASE-DIAGRAM OF PRASEODYMIUM

In this section we apply our LDA+GA implementation to the elemental praseodymium. As in Ref. 37, we employ the “standard” prescription for the double-counting functional and the general Slater-Condon parametrization of the on-site interaction assuming that the Hund’s coupling constant is $J = 0.7 \text{ eV}$ and that the value of the interaction-strength is $U = 6 \text{ eV}$, consistently with previous constrained LDA calculations.

The lattice-structure of the elemental praseodymium is dhcp at ambient conditions, and it undergoes the following sequence of transformations under pressure: dhcp $\rightarrow$ fcc $\rightarrow$ distorted-fcc $\rightarrow$ $\alpha$-U. While no appreciable volume collapse is associated with the transitions between the three lower-pressure phases — which are all characterized by relatively high symmetry and/or good packing ratios — the distorted-fcc $\rightarrow$ $\alpha$-U transition is accompanied by a sizable volume collapse (about 10% at room temperature).

It is widely believed that the low-symmetry $\alpha$-U lattice-structure in the elemental praseodymium is stabilized at high pressures by the delocalized $f$-electrons, according with a general argument based on the Peierls theorem, see Refs. 71, 72. The deformation from a high-symmetry structure to a low-symmetry structure can lower the bands-energy by opening a Peierls gap between a “bonding” band (below the Fermi level) and an “anti-bonding” band (above the Fermi level). This effect competes with the electrostatic Madelung interaction, which

\[ V^{\text{dc}}_i = \frac{dE^{\text{dc}}}{dN^{\text{loc}}_i} |_{N^{\text{loc}}_i = \langle \Phi_i \mid \sum \alpha \ c^\dagger_i \ c_i \mid \Phi_i \rangle}, \quad (70) \]

which determine the “correct” $V^{\text{dc}}_i$, and can be solved numerically, e.g., self-consistently, see Fig. 2.

E. A possible synergistic combination of LDA+GA and LDA+DMFT

In the previous subsection we have shown that the LDA+GA and the LDA+DMFT methods require, in order to determine the double-counting potentials $V^{\text{dc}}_i$ and the charge density $\rho(\mathbf{r})$, to solve iteratively multiple times the correlated Hubbard Hamiltonian [Eq. (63)].

We observe that, remarkably, the calculation of $V^{\text{dc}}_i$ and $\rho(\mathbf{r})$, as well as the total energy, does not require to compute the spectral properties of the system, but only the ground state.

Since the GA ground-state properties are generally in very good agreement with DMFT for the strongly correlated metals — even though the GA is much less computationally demanding, — this observation opens up the possibility to use the GA for structural relaxation and determine $V^{\text{dc}}_i$ and $\rho(\mathbf{r})$, and to perform a single DMFT iteration afterwards, in order to have access also to the spectral properties of the system of interest.
In order to further investigate the physics underlying the volume-collapse transition of praseodymium, in this work we study it theoretically in the fcc and α-U lattice-structures, see Fig. 3. The theoretical LDA and LDA+GA phase diagrams are shown in the lower panels of Fig. 3 in comparison with the experimental data. The theoretical pressure is obtained as \( P = -\frac{dE}{dV} \) from the corresponding total-energy curves, which are shown in the upper panels of Fig. 4. The agreement between the LDA+GA theoretical results and the experimental data is very good. Remarkably, the GA correction to the LDA total energy is very important for praseodymium, especially at low pressures. The LDA equilibrium point is about \( 20 \text{ Å}^3/\text{atom} \), while the experimental value is approximately \( 35 \text{ Å}^3/\text{atom} \), which is well reproduced by the LDA+GA calculation. Furthermore, while the LDA predicts that the α-U structure becomes less stable than the fcc phase only at negative pressures, the LDA+GA method predicts correctly that the volume collapse occurs at positive pressures, see the common tangent construction in the upper-right panel of Fig. 4.

In other words, in praseodymium the correlation effects favor energetically the fcc lattice-structure with respect to the α-U, stabilizing it at the equilibrium point and for a wide range of positive pressures. This fact is clearly illustrated also in the inset of the upper-right panel of Fig. 4 which represents the energy-difference between the fcc and α-U structures as a function of the volume, both in LDA and in LDA+GA. We point out that, contrarily to cerium, the fcc phase of praseodymium would not display any iso-structural volume-collapse transition by applying pressure. In fact, the second derivative of the fcc energy-volume curve is positive within the entire range of volumes considered.

Let us examine how the correlation effects taken into account by the GA correction influence the on-site \( f \) occupation-probabilities \( W_f \) and the \( f \) quasi-particle renormalization weights, which are determined as \( Z = \mathcal{R} \mathcal{R}^\dagger \) according to Eq. (41). In the upper panels of Fig. 5 the on-site \( f \) occupation-probabilities are illustrated for the fcc and for the α-U phases as a function of the volume. While the LDA probability distribution is very “broad” at all pressures, the LDA+GA probability distribution is relatively narrow, especially at large volumes, where we find that the majority of the \( f \)-electrons lie within the \( f^2 \) space, in agreement with recent experiments. The \( f \) quasi-particle renormalization weights are shown in the upper panels of Fig. 5. Note that, due to the spin-orbit coupling, the \( f \) quasi-particle weights are split in two groups with total angular momentum \( J = 5/2 \) and \( 7/2 \), respectively. While at small volumes both the \( Z \)’s decrease as a function of the volume, at larger volumes they develop a qualitatively different behavior: \( Z_{7/2} \) becomes significantly smaller than 1 — indicating that the system is very correlated in this regime, — and \( Z_{7/2} \) increases. This behavior is a consequence of the spin-orbit effect, which occurs also in cerium. In particular, \( Z_{7/2} \) grows because the \( 7/2 \) electrons disappear at larger vol-

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favors the high-symmetry lattice-structures such as the fcc. Nevertheless, there are few important aspects of the physics underlying the volume-collapse transition of praseodymium that are still not fully understood, and that require further investigation. (1) What is the role of the electron-correlations for the volume-collapse transition? (2) Would praseodymium display a volume-collapse transition even without taking into account the change of structure?
This is not surprising, as decreasing the distance between renormalization weights are considerably smaller than 1. Substantial at large volumes, where the quasi-particle renormalization to the pressure-volume phase-diagram becomes more small between the two lattice-structures.

Note that this consideration is consistent with the fact that, according to our calculations, the strength of the Peierls mechanism, which stabilizes the α-U phase, is very large volumes (negative pressures) the LDA total energy-difference captured by the LDA, and it is not directly related with the f-electron localization — which is substantial only at large volumes, as indicated by the f quasi-particle weights shown in the lower panels of Fig. 6.

In conclusion, we have observed that the behavior of the quasi-particle weights and of the f configuration-probabilities as a function of the volume is essentially equal for the fcc and the α-U lattice structures. In particular, at small volumes we find that Z ≃ 1, while at large volumes we find that Z ≪ 1. Consistently with the Peierls mechanism, while at small volumes the α-U has a lower energy, at large volumes the fcc becomes more stable. Since both the energy-difference between the two lattice structures is of the same order of magnitude for all volumes. Consequently, we shall attribute the consequent improved quantitative agreement with the experiments for the transition-volume to the overall more realistic evaluation of the total energy in LDA+GA with respect to LDA. In other words, we argue that the behavior of the energy-difference between the fcc and the α-U structures is essentially already qualitatively captured by the LDA, and it is not directly related with the f-electron localization — which is substantial only at large volumes, as indicated by the f quasi-particle weights shown in the lower panels of Fig. 6.

In conclusion, we have observed that the behavior of the quasi-particle weights and of the f configuration-probabilities as a function of the volume is essentially equal for the fcc and the α-U lattice structures. In particular, at small volumes we find that $Z \simeq 1$, while at large volumes we find that $Z \ll 1$. Consistently with the Peierls mechanism, while at small volumes the α-U has a lower energy, at large volumes the fcc becomes more stable. Since both the energy-difference between the two lattice structures and the quasi-particle weights are controlled by the volume, it is not surprising that the volume-collapse transition of praseodymium is accompanied by an abrupt delocalization of the f-electrons, and not even that a correlation between these two phenomena is found experimentally in several other rare-earth materials. On the other hand, based on our calculations, it does not seem appropriate to regard the above-mentioned
correlated as a general cause-effect relation. In fact, praseodimium would not display the transition without taking into account the change of structure (at least at small temperatures). Note also that other f-systems, such as Americium display volume-collapse structure-transitions maintaining essentially a constant f-valence, indicating that f-localization is not a crucial prerequisite for the volume-collapse transitions in f-systems.

VI. THE PRESSURE-VOLUME PHASE-DIAGRAM OF α-PLUTONIUM

Plutonium is the most exotic and complex metallic element in the periodic table, and many of its properties are still not well understood. The stable structure of plutonium at ambient conditions is α-Pu, that has a low-symmetry monoclinic structure, with 16 atoms within the unit cell grouped in 8 nonequivalent types, see Fig. 7. At higher temperatures, Pu can assume the following lattice structures: β (monoclinic, with 34 atoms within the unit cell grouped in 17 inequivalent types), γ (orthorhombic), δ (fcc), δ’ (bct), and ε (bcc).

It is widely accepted that several aspects of the phase-diagram of Pu relate with its position in the periodic table, which is midway through the so-called actinides-transition. In fact, Pu is the crossover element that terminates the series of light actinides, which are characterized by a strong involvement of the 5f electrons in the bonding, as opposed with Am and the heavier actinides. In particular, it is well understood that the fact that α-Pu and several other light actinides have such a low-symmetry lattice structure at ambient conditions arises from the participation of the f electrons to the metallic bond, and is a consequence of the Peierls instability, (see also the discussion of Pr discussed in the previous section).

The Peierls instability explains the low-symmetry lattice structures of α- and β-Pu as well as the large difference between their equilibrium volumes and the equilibrium volumes of the other phases. Note that these effects are qualitatively captured already by the LDA-like methods. On the other hand, despite the many efforts devoted to understand the phase diagram of Pu, there is currently no commonly accepted point of view on its electronic structure.

It is clear that, in order to be conclusive, the theoretical description of the electronic structure of Pu must be validated by first-principles calculations able to (I) reproduce correctly the experimental phase diagram and, at the same time, (II) take properly into account both the details of the bands structure and the f-electron correlations. The charge self-consistent LDA+DMFT potentially satisfies both of these requirements, and, in fact, it has enabled to understand several important properties of Pu. On the other hand, the LDA+DMFT calculations are very time-consuming for Pu — if used in combination with exact solvers such as continuous time quantum Monte Carlo (CTQMC)53 — which makes it practically impossible to calculate the total energy with good numerical precision for all phases and at many volumes. Fortunately, as we are going to show, these calculations are perfectly affordable with the charge self-consistent LDA+GA method. In this section we focus on α-Pu, which has been recently investigated within GGA+DMFT in Ref. 51. The other phases of Pu will be discussed in another publication.

As for the calculations of Pr discussed in the previous section, we employ the standard prescription for the double-counting and the general Slater-Condon parametrization of the on-site interaction. For α-Pu we perform calculations at (i) $J = 0.36 \text{eV}$, $U = 3 \text{eV}$, (ii) $J = 0.36 \text{eV}$, $U = 4.5 \text{eV}$ and (iii) $J = 0.51 \text{eV}$, $U = 4.5 \text{eV}$. Note that $J = 0.51 \text{eV}$ and $U = 4.5 \text{eV}$ are the same values previously assumed in Ref. 51. In our calculations we take into account all of the local many-body configurations with number of f electrons $0 \leq N \leq 9$. As we are going to show, taking into account such a broad range of local configurations is necessary to describe accurately the electronic structure and the total energy of α-Pu, especially at high pressures, where the system is more delocalized. In this work we do not perform structure relaxation, but we assume a uniform rescaling of the experimental lattice parameters at equilibrium.

The theoretical total energy of α-Pu is shown in the
In order to analyze the role of the \( f \) electron-correlations for the electronic structure of \( \alpha \)-Pu, in Fig. 9 we show the local configuration-probabilities \( f^n \) of each type of inequivalent atom as a function of the volume in LDA, GGA and LDA+GA. Our theoretical results are shown in comparison with the averaged \( f^4, f^5, f^6 \) configuration probabilities extrapolated from the X-ray absorption near-edge structure (XANES) measurements of Ref. 86. Remarkably, the agreement between our calculations and the experiments is very good. As expected, the LDA+GA probability distribution is much more narrow with respect to LDA, which confirms that the \( f \) electron-correlations are important in \( \alpha \)-Pu. On the other hand, it must be noted that, although the main valence configurations are \( f^4, f^5, f^6 \), also the other configuration probabilities — in particular \( f^7 \) — are not negligible. This observation proves that in order to describe properly the electronic structure of \( \alpha \)-Pu it is necessary to take into account a broad range of local configurations. Note that, surprisingly, the GGA probability distribution is very similar to LDA — and in disagreement with the experiments. This observation demonstrates that the electron correlations affect substantially the electronic structure of \( \alpha \)-Pu.

In the upper panels of Fig. 10 are shown the atom-dependent LDA+GA averaged quasi-particle weights. The quasi-particle weights indicate that, although the correlation effects are very important for the thermodynamical properties of Pu, the \( f \) electrons are delocalized. It must be pointed out that, while the GA ground-state expectation values are generally very accurate, the GA quasi-particle weights are systematically overestimated with respect to DMFT. On the other hand, our conclusion that the \( f \)-electrons are delocalized in \( \alpha \)-Pu is enforced also by the fact that the local \( f \)-configuration probability distribution shown in Fig. 9 is relatively broad, indicating a significant mixed-valence character. Note that, consistently with Ref. 51, the degree of correlation of the inequivalent atoms of \( \alpha \)-Pu relates with the number and relative distances of the nearest-neighbor atomic positions. It is worth pointing out that \( Z \) would have been considerably underestimated if the range of valence configurations taken into account was truncated, as it is often done in several methods in order to speed-up the calculations. For instance, if only \( f^4, f^5, f^6 \) are taken into account \( Z \) is underestimated by \(~ 20 \% \). This confirms that in order to describe properly the electronic structure of \( \alpha \)-Pu it is necessary to take into account a broad range of local configurations.

In the lower panels of Fig. 10 are shown the orbital populations of the \( 5/2 \) and \( 7/2 \) \( f \)-electrons. In order to compare our theoretical results with the experiments, we calculate the so called branching ratio \( B \) — that is a measure of the strength of the spin-orbit coupling interaction within the \( f \) shell. The value of \( B \) is calculated independently for each inequivalent atom making use of...
FIG. 9: (Colors online) Evolution as a function of the volume of the atom-dependent LDA (left panel) and LDA+GA (right panel) on-site $f$ occupation-probabilities of $\alpha$-Pu. Our results are shown in comparison with the occupation probabilities for $f^5$ (diamond), $f^6$ (square) and $f^4$ (circle) extrapolated from the XANES measurements at ambient conditions of Ref. 91. The labels of the atoms refer to Fig. 7.

FIG. 10: (Colors online) Evolution as a function of the volume of the atom-dependent LDA+GA quasi-particle renormalization weights $Z$ (upper panel) of the $5/2$ (continuous lines) and $7/2$ (dotted lines) $f$-electrons and corresponding orbital occupations (lower panel) for $\alpha$-Pu.

| $U$ | $J$ | $B_{5/2}$ | $B_{7/2}$ | $B_{exp}$ |
|-----|-----|----------|----------|----------|
| 4.5eV | 0.51eV | 0.51 | 0.50 | 0.51 |
| 3.0eV | 0.36eV | 0.36 | 0.35 | 0.36 |

the equation

$$B = \frac{3}{5} - \frac{4}{15} \frac{1}{14 - n_{5/2} - n_{7/2}} \left( \frac{3}{2} n_{7/2} - 2 n_{5/2} \right),$$

which was first derived in Ref. 93. In Table I the theoretical equilibrium values of $B$ are reported in comparison with the data of Ref. 92 which were extrapolated from electron energy-loss spectroscopy (EELS) and X-ray absorption spectroscopy (XAS) experiments. Our theoretical results are in good agreement with the experiments for all values of $U$ and $J$ considered, and indicate
that most of the \( f \) electrons of \( \alpha \)-Pu have 5/2 character because of the spin-orbit effect.

It is remarkable that each one of our LDA+GA charge self-consistent calculations of \( \alpha \)-Pu has been performed on a single computer node with 8 cores, and converged in less than 3 days. Note that, instead, for the LDA+DMFT calculations of Ref. 51 it has been necessary to completely dedicate for more than 3 months an entire cluster with 24 computer nodes, each one with 12 cores. Each LDA+GA calculation has required about 10 charge iterations.

In conclusion, we have computed the zero-temperature pressure-volume phase diagram, the \( f \) occupation probabilities and other properties of \( \alpha \)-Pu, finding a very good agreement with the experiments. Our calculations indicate that although the \( f \)-electrons are delocalized, the (atom-selective) correlations are crucial in order to describe properly the electronic structure and the thermodynamical properties of \( \alpha \)-Pu.

VII. CONCLUSIONS

We have developed an exceptionally efficient algorithm to implement the GA. Furthermore, we have derived a functional formulation of LDA+GA that has the same mathematical structure of LDA+DMFT. This insight has enabled us to pattern the LAPW interface between LDA and GA after the LDA+DMFT work of Ref. 13.

Using our LDA+GA code, we have performed first-principles calculations of Pr and \( \alpha \)-Pu under pressure, which are prototypical systems with partially localized \( f \) electrons.

Our calculations of Pr indicate that the volume-collapse transition of prasiddiuminium is not driven by the concomitant delocalization of the \( f \) electrons. In fact, contrarily to cerium, the system would not display any volume-collapse transition without taking into account the change of lattice structure (at least at small temperatures). This suggests that there are no reasons to exclude that, in other \( f \) materials, a volume-collapse transition may occur without any concomitant substantial \( f \)-delocalization — as indicated, for instance, by recent experiments on the elemental Americium. Note that the understanding of the connection between \( f \)-delocalization and volume-collapse transitions in \( f \) systems is one of the most important puzzles in condensed matter theory.

Our calculations of \( \alpha \)-Pu under pressure constitute the first theoretical description of this material providing good agreement with all of the available experiments — including both the thermodynamical properties and the \( f \) occupation-probabilities. Our results indicate that, although the \( f \) electrons are very delocalized in this phase, the electron-correlations affect substantially the electronic structure and the thermodynamical properties of Pu. From the technical point of view, these calculations clearly demonstrate the exceptional capabilities of the computational scheme presented in this work. Indeed, our method enables us to perform rapidly accurate first-principles calculations of strongly correlated materials even for systems so complex that other state-of-the-art methods are so time-consuming to not be practically applicable.

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Appendix A: Summary formulation of the Gutzwiller variational method

For completeness, the derivation of the Lagrange formulation of the GA [Eq. 6] — that we employed in Sec. II as a starting point — is summarized in this appendix. The material presented in this appendix makes large use of ideas developed in previous works by several authors.

1. Standard formulation

Let us write the Hubbard Hamiltonian in an infinite-coordination lattice, see Eq. (1), in the form

\[
\hat{H} = \sum_{kij,\alpha\beta} \epsilon_{kij}^{\alpha\beta} \hat{c}_{kij}^{\dagger} \hat{c}_{kij}^{\alpha\beta} + \sum_{\Gamma} \sum_{\Gamma'} \sum_{M} [H_{\Gamma\Gamma'}^{loc}]_{\Gamma\Gamma'}^{\Gamma\Gamma} |\Gamma, \Gamma'\rangle \langle \Gamma, \Gamma'| ,
\]

(A1)

where here, in order to derive our formalism, we assume conveniently that \(|\Gamma, \Gamma'\rangle\) are local Fock states

\[
|\Gamma, \Gamma'\rangle = [\epsilon_{R1}^{\dagger}]_{\Gamma\Gamma'}^{n_1} \cdots [\epsilon_{RM}^{\dagger}]_{\Gamma\Gamma'}^{n_M} |0\rangle .
\]

(A2)

From now on we will name the above \( c \) basis-set the original basis.

The structure of the Gutzwiller variational function is given by Eq. (3), where |\( \Psi_0 \rangle\) is an uncorrelated variational wavefunction, that satisfies Wick’s theorem, and \( \mathcal{P}_{\Gamma\Gamma'} \) is a general operator acting on the local configurations at the site \((R, i)\), which we represent in the original basis as follows

\[
\mathcal{P}_{\Gamma\Gamma'} = \sum_{\Gamma\Gamma'} |A_{\Gamma\Gamma'}\rangle \langle \Gamma, \Gamma'| \Gamma' , \Gamma\rangle.
\]

(A3)
The variational problem to solve amounts to variationally determine both $|\Psi_0\rangle$ and $\mathcal{P}_R$ by minimizing the average value of $\mathcal{H}$

$$\mathcal{E}[\Psi_0, \Lambda] = \frac{1}{N} \langle \Psi_0 | \mathcal{P}_G^\dagger \mathcal{H} \mathcal{P}_G | \Psi_0 \rangle \quad (A4)$$

within the manifold of parameters that satisfy the Gutzwiller constraints, see Eqs. [4]-[5].

2. Reformulation of the Gutzwiller problem

In this section we briefly summarize the reformulation of the Gutzwiller problem derived in Refs. [25, 26].

a. The mixed-basis representation

Let us consider the matrix

$$\langle \Psi_0 | \hat{c}_{\Gamma,Ri} \hat{c}_{\Gamma',Ri} | \Psi_0 \rangle \equiv [\rho^\alpha_{\beta}]:_{\alpha \beta} \quad (A5)$$

Since $\rho^\alpha_{\beta}$ are Hermitian, there always exists a unitary transformation $\mathcal{U}_t$ that diagonalizes it, i.e., such that

$$\hat{f}_{\Gamma,Ri} = \sum_\alpha [\mathcal{U}_t]_{\alpha \alpha} \hat{c}_{\Gamma,Ri}^\dagger \quad (A6)$$

$$\langle \Psi_0 | \hat{f}_{\Gamma,Ri} \hat{f}_{\Gamma',Ri} | \Psi_0 \rangle \equiv [\rho^\alpha_{\beta}]:_{\alpha \beta} = \delta_{\alpha \beta} [\rho^\alpha_{\beta}]:_{\alpha \beta} \quad (A7)$$

The so obtained ladder operators $\hat{f}_{\Gamma,Ri}$ are named natural-basis operators.

Note that the connection between the contracted natural basis $\Gamma$ and the original basis $c$ depends only on $|\Psi_0\rangle$. At given $|\Psi_0\rangle$ the coefficients $\Lambda$ that determine the Gutzwiller projector, see Eq. [A3], are free variational parameters.

Instead of expressing the Gutzwiller projector in terms of the original basis as in Eq. (A3), it is convenient to adopt the following mixed-basis representation

$$\hat{P}_G = \sum_{\Gamma n} |\hat{f}_{\Gamma,Ri}^\dagger|^n \hat{f}_{\Gamma,Ri}^\dagger |n, R_i \rangle$$

where $|\Gamma, R_i \rangle$ are Fock states in the original basis, see Eq. [A2], while $|n, R_i \rangle$ are Fock states in the natural basis, represented as

$$|n, R_i \rangle = \hat{f}_{\Gamma,Ri}^\dagger n \hat{f}_{\Gamma,Ri}^\dagger M |0\rangle \quad (A8)$$

For later convenience we adopt the convention that the order of the $|\Gamma, R_i \rangle$ and the $|n, R_i \rangle$ states is the same. For instance, if the second $\Gamma$-vector in Eq. (A8) is $\hat{c}_{1R}^\dagger \hat{c}_{2R}^\dagger |0\rangle$ then the second $n$-vector is $\hat{f}_{1R}^\dagger \hat{f}_{2R}^\dagger |0\rangle$.

As we are going to see, the mixed-basis parametrization of the Gutzwiller projector enables us to gauge-away from the formalism the unitary matrix $\mathcal{U}$ that relates the original basis and the natural basis, see Eq. [A7], which is a great simplification.

b. Gutzwiller expectation values

In an infinite-coordination lattice the expectation value of any observable can be computed analytically.

Let us define the uncorrelated occupation-probability matrices $P^\alpha_{\beta}$ with elements

$$[P^\alpha_{\beta}]_{nn'} \equiv \langle \Psi_0 | \hat{n}', \hat{R}_i | n, \hat{R}_i | \Psi_0 \rangle = \delta_{nn'} \prod_{a=1}^M \left( [n^0_{\alpha a}]_{aa} \right)^{n_a} \left[ 1 - [n^0_{\alpha a}]_{aa} \right]^{1-n_a} \quad (A10)$$

We also introduce the matrix representations of the operators $\hat{f}_{\Gamma,Ri}$ and $\hat{c}_{\Gamma,Ri}$

$$[F^\alpha_{\beta}]_{nn'} = \langle n, \hat{R}_i | \hat{f}_{\Gamma,Ri} \hat{f}_{\Gamma',Ri} | n', \hat{R}_i \rangle \quad (A11)$$

Note that, since we have assumed that the order of the $|\Gamma, \hat{R}_i \rangle$ and the $|n, \hat{R}_i \rangle$ states is the same, the matrix elements of $\hat{f}_{\Gamma,Ri}$ can be equivalently computed as

$$[F^\alpha_{\beta}]_{\Gamma \Gamma'} = \langle \Gamma, \hat{R}_i | \hat{f}_{\Gamma,Ri} \hat{f}_{\Gamma',Ri} | \Gamma', \hat{R}_i \rangle \quad (A12)$$

With the above definitions, it can be readily verified that the expectation value of any local observable can be calculated as

$$\langle \Psi_0 | \hat{P}_{\Gamma} \hat{A}_{\hat{R}_i} \mathcal{P}_{\Gamma} \hat{P}_{\Gamma} | \Psi_0 \rangle = \text{Tr}[P^\alpha_{\beta} \hat{A}^\dagger_\alpha \hat{A}^\dagger_\beta] \quad (A13)$$

where

$$\text{Tr}[P^\alpha_{\beta} \hat{A}^\dagger_\alpha \hat{A}^\dagger_\beta] = 1 \quad (A15)$$

$$\text{Tr}[P^\alpha_{\beta} \hat{A}^\dagger_\alpha F^\dagger_{\Gamma,Ri} F^\dagger_{\Gamma',Ri}] = \langle \Psi_0 | \hat{f}_{\Gamma,Ri}^\dagger \hat{f}_{\Gamma',Ri}^\dagger | \Psi_0 \rangle \quad (A16)$$

The average of the inter-site density matrix reduces to calculate

$$\langle \Psi_0 | \hat{P}_{\Gamma} \hat{c}_{\Gamma,Ri} \hat{c}_{\Gamma',Ri} \hat{P}_{\Gamma} | \Psi_0 \rangle \quad (A17)$$

$$= \sum_{ab} \langle \Psi_0 | [\mathcal{R}]_{a0} \hat{f}_{\Gamma,Ri}^\dagger \mathcal{R}^\ast_{\beta 0} \hat{f}_{\Gamma',Ri}^\dagger | \Psi_0 \rangle \quad (A18)$$

In other words, the mixed-basis single-particle density matrix averaged over $|\Psi_0\rangle$ is computed by averaging over $|\Psi_0\rangle$ a renormalized density matrix with natural Fermionic operators, replacing the physical ones according to the rule

$$\hat{c}_{\Gamma,Ri}^\dagger \rightarrow \sum_a [\mathcal{R}]_{a\alpha} \hat{f}_{\Gamma,Ri}^\dagger \quad (A19)$$

Within the definitions given in this section, it can be shown that the renormalization matrices $\mathcal{R}$ can be expressed as

$$[\mathcal{R}]_{a\alpha} = \text{Tr}[P^\alpha_{\beta} \hat{f}_{\Gamma,Ri}^\dagger \hat{f}_{\Gamma,Ri}^\dagger \hat{F}_i^\dagger] / [n^0_{\alpha a}]$$

Note that, thanks to the mixed-basis representation of the Gutzwiller projector, the unitary transformation that relates the natural-basis operators $f$ to the original ones $c$ needs not to be known explicitly, which is a great simplification.
The formalism can be further simplified by defining the following matrix:

$$\phi_i = \lambda_i \sqrt{P_i^0}.$$  

(A20)

Within this definition, the expectation value of any local observable, see Eq. \([A13]\), reduces to

$$\langle \Psi_0 | \hat{P}_G^\dagger \hat{A}_R \hat{P}_G | \Psi_0 \rangle = \text{Tr} \left[ \phi_i^\dagger \phi_i^\dagger A_i \right];$$  

(A21)

and it has to be minimized fulfilling Eqs. \([A22]-[A24]\).

Following Refs. \([25,29]\) we take into account the constraints by applying the theorem of the Lagrange multipliers as follows

$$\mathcal{L}[\Psi_0, E; \phi, E^c; \mathcal{R}, \mathcal{R}^\dagger, \lambda, \eta; \mu; \mathcal{D}, \mathcal{D}^\dagger, \chi; n^0] =$$

\[\frac{1}{N} \sum_{k,i,j} \left[ \mathcal{R}_i \chi_{k,i,j} \right]_{ab} \langle \Psi_0 | \hat{f}_{kia} \hat{f}_{kjb} | \Psi_0 \rangle + \sum_i \text{Tr} \left[ \phi_i^\dagger H_i^{loc} \right] + \] 

\[E(1 - \langle \Psi_0 | \Psi_0 \rangle) + \sum_i \mathcal{E}_i^c \left( 1 - \text{Tr} \left[ \phi_i^\dagger \phi_i \right] \right) + \] 

\[\sum_i \sum_{\alpha\beta} [\mathcal{D}_i]_{\alpha\alpha} \left( \text{Tr} \left[ \phi_i^\dagger F_{i\alpha} \phi_i F_{i\alpha} \right] - [\mathcal{R}_i]_{\alpha\alpha} \right) + \] 

\[\sum_i \sum_{\alpha\beta} [\lambda^\dagger_i]_{\alpha\beta} \left( \text{Tr} \left[ \phi_i^\dagger F_{i\alpha} \phi_i F_{i\beta} \right] - [\eta_i]_{\alpha\beta} \right) + \] 

\[\sum_i \sum_{R_{\iota,\alpha\neq\beta}} [\lambda_{\iota}]_{\alpha\beta} \langle \Psi_0 | \hat{f}_{R_{\iota}a} \hat{f}_{R_{\iota}b} | \Psi_0 \rangle - [\eta_i]_{\alpha\beta} \] 

(A26)

Note that \(n_i^0\) and \(R_{\iota}\) have been conveniently promoted to independent variables. Within this formulation, the numerical problem arising from the stationarity condition of \(\mathcal{L}\) is particularly easy to solve numerically, see Sec. \(IIC\)

It is convenient to rewrite Eq. \([A26]\) as follows

\[\mathcal{L}[\Psi_0, E; \phi, E^c; \mathcal{R}, \mathcal{R}^\dagger; \lambda + \eta; \mu; \mathcal{D}, \mathcal{D}^\dagger, \chi; n^0] = \frac{1}{N} \langle \Psi_0 | \hat{H}_G^{pp} | \mathcal{R}, \mathcal{R}^\dagger; \lambda + \eta \rangle | \Psi_0 \rangle + E(1 - \langle \Psi_0 | \Psi_0 \rangle) + \] 

\[\sum_i \text{Tr} \left[ \phi_i^\dagger H_i^{loc} + \sum_{\alpha\beta} \left[ (\mathcal{D}_i]_{\alpha\alpha} \phi_i^\dagger F_{i\alpha} \phi_i + \text{H.c.} \right] + \sum_i \sum_{\alpha\beta} [\lambda_i]_{\alpha\beta} \phi_i^\dagger \phi_i F_{i\alpha} F_{i\beta} \right] + \] 

\[\sum_i \sum_{\alpha\beta} [\lambda_{\iota}]_{\alpha\beta} \left[ (\mathcal{R}_i]_{\alpha\alpha} [\mathcal{R}_i]_{\alpha\alpha} + \text{c.c.} \right] \sqrt{[\eta_i]_{\alpha\beta} \left( 1 - [\eta_i]_{\alpha\beta} \right)} \] 

(A27)

where

\[\hat{H}_G^{pp}[\mathcal{R}, \mathcal{R}^\dagger; \lambda + \eta] \equiv \frac{1}{N} \sum_{k,i,j} \left[ \mathcal{R}_i \chi_{k,i,j} \right]_{ab} \hat{f}_{kia} \hat{f}_{kjb} + \sum_i \sum_{R_{\iota,\alpha\neq\beta}} [\lambda_{\iota}]_{\alpha\beta} \hat{f}_{R_{\iota}a} \hat{f}_{R_{\iota}b} \] 

(A28)

is the GA quasi-particle Hamiltonian of the system.
Let us now consider a generic Impurity Anderson Model relates with the Luttinger’s sum rule, as discussed at the commutes with the number operator \( \hat{n} \) because we have assumed that the Gutzwiller projector \( \hat{P}_G \) has been imposed on

\[
\sum_i \left[ \sum_{ab} \left( \langle \lambda \rangle_{ab} + \langle \lambda^* \rangle_{ab} \right) n_{ab} + \sum_{aa} \langle \lambda \rangle_{aa} \right] + \mu N ,
\]

where

\[
\hat{H}^{\text{imp}}[\mathcal{R}, \mathcal{R}^\dagger; \lambda + \eta; \mu] \equiv \sum_{i} \sum_{ab} \left[ \mathcal{R}_i \epsilon_{k,i} \mathcal{R}_i^\dagger \right]_{ab} \hat{f}_i^{\dagger} \hat{f}_j + \hat{\mathcal{H}}^{\text{loc}}[\{ b^\dagger_a \}, \{ b_a \}],
\]

Note that the constraint on the number of particles has been imposed on \( |\Psi_0\rangle \) instead of \( |\Psi_G\rangle \). This is licit because we have assumed that the Gutzwiller projector \( \hat{P}_G \) commutes with the number operator \( \hat{N} \). This condition relates with the Luttinger’s sum rule, as discussed at the end of Sec. III

**Appendix B: Application to impurity models**

In the previous section we have discussed our method to solve the GA equations for a generic Hubbard model. Let us now consider a generic Impurity Anderson Model (IAM)

\[
\hat{h} = \sum_i c_i a_i^\dagger a_i + \sum_{ia} \frac{V_{ai}}{\sqrt{\mathcal{R}}} b_i^\dagger a_i + \text{H.c.} + \hat{\mathcal{H}}^{\text{loc}}[\{ b^\dagger_a \}, \{ b_a \}],
\]

where \( \hat{\mathcal{H}}^{\text{loc}} \) is the Hamiltonian of the impurity, which includes both the interaction and the one-body component. The purpose of this section is to solve \( \hat{h} \) within the GA in the grand-canonical ensemble.

We observe that any IAM can be viewed as a special Hubbard model, where no translational invariance is assumed and only the impurity site is correlated. In this special case the GA equations derived in the previous section reduce to

\[
\mathcal{T} \sum_n \left[ \frac{1}{\mathcal{R}} \hat{G}(z_n) \right]_{ab} = 0 \quad \forall a \neq b \quad \text{(B2)}
\]

\[
\frac{1}{2} + \mathcal{T} \sum_n \left[ \frac{1}{\mathcal{R}} \hat{G}(z_n) \right]_{ba} = n_{0}^{ab} \quad \text{(B3)}
\]

\[
\mathcal{T} \sum n \Delta(z_n) \hat{G}(z_n) \left[ \frac{1}{\mathcal{R}} \right]_{aa} = D_{aa} \sqrt{n_{0}^{aa} (1-n_{0}^{aa})} \quad \text{(B4)}
\]

\[
\frac{n_{0}^{ab} - \frac{1}{\mathcal{R}}} {\sqrt{n_{0}^{ab} (1-n_{0}^{ab})}} \sum_{\alpha} D_{aa} \mathcal{R}_{aa} + \text{c.c.} \quad \delta_{ab} - [\lambda+\lambda^*]_{ab} = 0 \quad \text{(B5)}
\]

\[
\hat{H}^{\text{emb}}[\mathcal{D}, \mathcal{D}^\dagger; \lambda^*] |\Phi\rangle = \mathcal{E}^* |\Phi\rangle \quad \text{(B6)}
\]

\[
\mathcal{F}^{(1)}_{\text{ab}} \equiv \langle \Phi | \hat{c}_{a}^{\dagger} \hat{c}_{a} | \Phi \rangle - [\mathcal{R}]_{aa} \sqrt{n_{0}^{aa} (1-n_{0}^{aa})} = 0 \quad \text{(B7)}
\]

\[
\mathcal{F}^{(2)}_{\text{ab}} \equiv \langle \Phi | \hat{f}_{b} \hat{f}_{a}^{\dagger} | \Phi \rangle - n_{0}^{ab} = 0 , \quad \text{(B8)}
\]

where

\[
\mathcal{R} \equiv \frac{1}{\mathcal{R}} - \frac{\lambda}{\mathcal{R}^\dagger} + \frac{1}{\mathcal{R}} (\lambda + \eta) \frac{1}{\mathcal{R}^\dagger} \quad \text{(B12)}
\]

is the hybridization function

\[
\mathcal{G}(z) = \frac{1}{z - \Delta(z) - \Sigma(z)} \quad \text{(B11)}
\]

is the coherent part of the impurity Green’s function, and

\[
\Sigma(z) \equiv - \mathcal{R} \mathcal{F}^{(1)} + \mathcal{F}^{(1)} + \frac{\lambda + \eta}{\mathcal{R}^\dagger} \quad \text{(B12)}
\]

is the Gutzwiller self-energy of the impurity (that includes also the on-site energies in our notation).

Note that, since now we are working in the grand-canonical ensemble, there is no analog to Eq. (20) in Eqs. (B2)-(B11).

For later convenience, we observe that the impurity quasi-particle Green’s function that corresponds to Eq. (B11) is given by

\[
\hat{G}^{\text{qp}}(z) \equiv \frac{1}{\mathcal{R}} \mathcal{G}(z) \frac{1}{\mathcal{R}} = \frac{1}{z - \mathcal{R} \Delta(z) \mathcal{R}^\dagger - \lambda - \eta} . \quad \text{(B13)}
\]
1. The algorithm

As for the Hubbard model, the above equations can be solved as follows. (i) Given \((\mathcal{R}, \lambda)\), we use Eq. (B2) to compute the Lagrange multipliers \(\eta\) and the corresponding impurity Green’s function \(\mathcal{G}\), which determines \(n^0\) through Eq. (B3), \(\mathcal{D}\) through Eq. (B4), and \(\lambda^0\) through Eq. (B5). (ii) Thereafter, we solve the embedding Hamiltonian, see Eq. (B6), to compute \(|\Phi\rangle\), which determines the left members of Eqs. (B7) and (B8). The equations (B7) and (B8) are verified if and only if \((\mathcal{R}, \lambda)\) is the correct set of variational parameters, satisfying the vector-equation

\[
\left(\mathcal{F}^{(1)}[\mathcal{R}, \lambda], \mathcal{F}^{(2)}[\mathcal{R}, \lambda]\right) = 0.
\]

(B14)

Note that, since we have used \(\mathcal{G}\) in Eqs. (B2)–(B4), the GA equations depend explicitly only on the hybridization function \(\Delta(z)\), and on the impurity Hamiltonian \(\mathcal{H}_{\text{loc}}\).
