Lattice density functional theory of the single-impurity Anderson model: Development and applications

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A lattice density functional theory (LDFT) of the single-impurity Anderson model is presented. In this approach the basic variable is the single-particle density matrix γ_{ij} with respect to the lattice sites and the fundamental unknown functional is the Coulomb interaction energy $W[\gamma]$. Using general symmetry properties, a two-level ansatz for $W[\gamma]$ in spin-restricted systems is proposed which involves explicitly only the impurity orbital and a single symmetry-adapted conduction-band state. A simple analytical functional dependence of $W[\gamma]$ is derived on the basis of exact results of this two-level problem. The resulting approximation is shown to be exact in two important opposite limits: a totally degenerate conduction band and a conduction band with widely separated discrete levels. Applications to finite rings having $N \leqslant 100$ atoms yield very accurate results for ground-state properties such as the kinetic, interaction, and total energy, as well as the occupation and magnetic moment of the local impurity orbital. This holds for all considered interaction strengths, from weak to strong correlations, as well as in the Kondo and intermediate valence regimes. One concludes that the present two-level approximation provides an appropriate framework for investigating subtle electron-correlation effects of the Anderson model within LDFT.

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I. INTRODUCTION

Density functional theory (DFT) is presently the most efficient method of determining the electronic properties of matter from first principles.[1] In this theory, originally formulated by Hohenberg and Kohn, the electron density $\rho(\vec{r})$ replaces the wave function as the basic unknown of the many-body problem.[2] Practical calculations are usually based on the Kohn-Sham scheme which reduces the interacting many-body problem to a set of self-consistent single-particle equations.[3] In principle, this transformation is exact, thus allowing one to take into account all electronic correlations. However, the universal interaction-energy functional $W[\rho(\vec{r})]$ is unknown and the results of applications consequently depend on the available approximations. Most commonly, the local density approximation (LDA),[3] the spin-polarized local spin-density approximation (LSDA),[4] and the generalized gradient approximation (GGA)[5] are used. The former were originally derived from exact solutions for the homogeneous electron gas, whereas the latter incorporates effects of inhomogeneous electron densities. Although successful in countless applications, these approximations are not suitable for explaining the effects of strong electronic correlations as found, for example, in heavy fermion materials, high-temperature superconductors, or Mott insulators.[6,7]

The large majority of theoretical approaches to investigate strongly correlated systems start from tight-binding model Hamiltonians on discrete lattices, e.g., the Hubbard and the Anderson model,[8,9] and incorporate the localized character of electronic states by means of a strong local Coulomb repulsion. In past years significant progress has been achieved in the development of the density functional theory of many-body models, basically concerning the Hubbard and Anderson models in different dimensions.[10–16] Lattice density functional theory (LDFT) has been developed in order to address the challenges of the physics of these models and to gain insight into the exchange and correlation energy functional for realistic strongly correlated systems. Thus, the possibility of studying many-body lattice Hamiltonians in the framework of density functional theory has been opened. In this approach the single-particle density matrix $\gamma_{ij\sigma}$ with respect to the lattice sites ij and the spin σ replaces the wave function as the basic variable of the many-body problem. As in any density functional approach it is essential, for the practicability of any study of physical properties, to derive accurate approximations to the kinetic energy and interaction-energy functionals $T[\gamma]$ and $W[\gamma]$. The approximate functionals derived for the Hubbard model have been shown to give an accurate qualitative and quantitative description of the most important ground-state properties, including in particular the ground-state kinetic and correlation energies, charge-excitation gaps, dimerization energies, and charge susceptibilities.[14] The good agreement with available analytical and numerical results (Bethe ansatz, exact diagonalization, density-matrix renormalization group, and Monte Carlo methods) has demonstrated that LDFT is an efficient tool for determining electronic properties of many-body lattice models.

The purpose of this work is to develop the LDFT of the single-impurity Anderson model whose properties cannot be understood in terms of mean-field approximations and therefore require a rigorous description of charge and spin fluctuations.[17] Consequently, electron correlations are expected to play a central role in the derivation of accurate approximations to $W[\gamma]$. Hennig and Carlsson proposed an energy functional for the Anderson model based on an implicit inequality for the interaction energy.[13] This led to the so-called second-moment approximation which can be shown to be exact in the case of a two-level system. Using this implicit approximation to the correlation energy for small clusters, Hennig and Carlsson obtained accurate results for the energy, one-electron properties, and charge and spin fluctuations of Anderson impurities. In our work an alternative approach is proposed which allows us to derive an

explicit analytical form for the interaction-energy functional $W[\gamma]$. This approximation takes advantage of the invariance of $W[\gamma]$ with respect to unitary transformations within the conduction-band states and also recovers the exact functional dependence in some important limits.

The remainder of the paper is organized as follows. In Sec. II the basic framework of the density functional theory of the single-impurity Anderson model is presented. This is followed by the derivation and discussion of some general properties of the fundamental interaction-energy functional $W[\gamma]$ (Sec. III). Based on these properties and on the exact solution of the two-level Anderson problem, we introduce in Sec. IV an explicit approximation to $W[\gamma]$, which can be applied to arbitrary lattices and band fillings. Here, we show that the approximation is exact both in the limit of a totally degenerate conduction band and in the limit of widely separated discrete conduction-band levels. In Sec. V one- and two-dimensional systems are considered as application of the method. Results are given for several properties of finite Anderson rings and periodic square clusters such as the ground-state energy, the kinetic and Coulomb contributions, the impurity valence, and local moments. The full range of model parameters is explored from weak to strong correlations, integer to intermediate valence, narrow to wide conduction band, and even as a function of ring length. The results are systematically compared with exact Lanczos diagonalizations,[18] whenever available, in order to assess the accuracy of our two-level approximation and reveal its possible limitations. Finally, Sec. VI summarizes the main conclusions and points out some relevant future extensions.

II. DENSITY-FUNCTIONAL THEORY OF THE SINGLE-IMPURITY ANDERSON MODEL

The essential low-energy physics of magnetic impurities in normal metals is expected to be described by the Anderson model,[9] which can be written as

$$\hat{H} = \hat{H}_{\rm cond} + \hat{H}_{\rm imp} + \hat{W}. \tag{1}$$

The first term

$$\hat{H}_{\rm cond} = \sum_{\mathbf{k}\sigma} \varepsilon_{\mathbf{k}} \hat{c}^{\dagger}_{\mathbf{k}\sigma} \hat{c}_{\mathbf{k}\sigma} \tag{2}$$

represents the single-particle electronic structure of the relevant valence electrons in the host metal. As usual, $\hat{c}^{\dagger}_{\mathbf{k}\sigma}$ ($\hat{c}_{\mathbf{k}\sigma}$) denotes the creation (annihilation) operator for an electron with spin $\sigma = \uparrow$ or $\downarrow$ in the conduction-band state with energy $\varepsilon_{\mathbf{k}}$. Notice that Eq. (2) can be written as

$$\hat{H}_{\rm cond} = \sum_{i\sigma} \varepsilon^{s}_{i} \hat{a}^{\dagger}_{i\sigma} \hat{a}_{i\sigma} + \sum_{ij\sigma} t_{ij} \hat{a}^{\dagger}_{i\sigma} \hat{a}_{j\sigma} \tag{3}$$

in terms of the atomic s orbitals $\hat{a}^{\dagger}_{i\sigma}$ at site i, the corresponding s level ε^{s}_{i}, and the nearest-neighbor (NN) hopping integral t_{ij} (typically $t_{ij} = -t < 0$ for all NN ij). The second term in Eq. (1) describes the single-particle contributions involving the magnetic impurity orbital and is given by

$$\hat{H}_{\rm imp} = \sum_{\sigma} \varepsilon_{f} \hat{n}_{f\sigma} + \sum_{\mathbf{k}\sigma} V_{\mathbf{k}f} (\hat{c}^{\dagger}_{\mathbf{k}\sigma} \hat{f}_{\sigma} + \hat{f}^{\dagger}_{\sigma} \hat{c}_{\mathbf{k}\sigma}), \tag{4}$$

where $\hat{f}^{\dagger}_{\sigma}$ creates an electron with spin σ in the localized f orbital having an energy ε_f ($\hat{n}_{f\sigma} = \hat{f}^{\dagger}_{\sigma} \hat{f}_{\sigma}$). The hybridization energy $V_{\mathbf{k}f}$ scales linearly with the local hybridization parameter V_{sf} between the s and the f orbitals at the impurity atom. Finally, the third term

$$\hat{W} = U \hat{n}_{f\uparrow} \hat{n}_{f\downarrow} \tag{5}$$

takes into account the dominant Coulomb interaction between two electrons occupying the localized f orbital. The model reflects the interplay between reducing ground-state average of $\hat{W}$ by developing a correlated state that minimizes the double occupations $\langle \hat{n}_{f\uparrow} \hat{n}_{f\downarrow} \rangle$ on the f orbital, and favoring electronic hoppings between the f orbital and the conduction-band states. The latter are triggered by the hybridizations $V_{\mathbf{k}f}$ in Eq. (4) and are generally accompanied by an increase of $\langle \hat{n}_{f\uparrow} \hat{n}_{f\downarrow} \rangle$.

In the Anderson model the single-particle band structure $\varepsilon_{\mathbf{k}}$ (or equivalently, the s orbital energies ε^{s}_{i} and interatomic hoppings t_{ij}), ε_f, and $V_{\mathbf{k}f}$ define the system under study and thus play the role of the external potential $v_{\rm ext}(\vec{r})$ in conventional DFT. These parameters enter in the expression for the ground-state energy in a bilinear form together with the single-particle density matrix elements $\gamma_{\mathbf{k}\mathbf{k}'\sigma}$, $\gamma_{\mathbf{k}f\sigma}$, and $\gamma_{ff\sigma}$. Therefore, the basic variable of LDFT is the full single-particle density matrix γ.

A formal way of extending DFT to lattice models is to demonstrate the Hohenberg-Kohn (HK) theorem for a general many-body Hamiltonian of the form

$$\hat{H} = \hat{T} + \hat{W} = \sum_{\alpha\beta\sigma} t_{\alpha\beta}\, \hat{c}^{\dagger}_{\alpha\sigma} \hat{c}_{\beta\sigma} + \sum_{\substack{\alpha\beta\gamma\delta \\ \sigma\sigma'}} V^{\sigma\sigma'}_{\alpha\beta\gamma\delta} \hat{c}^{\dagger}_{\alpha\sigma} \hat{c}^{\dagger}_{\beta\sigma'} \hat{c}_{\delta\sigma'} \hat{c}_{\gamma\sigma}, \tag{6}$$

where $\hat{c}^{\dagger}_{\alpha\sigma}$ creates an electron with spin σ at the lattice site α. The theorem states that for nondegenerate ground states $|\Psi\rangle$ the mapping between $|\Psi\rangle$ and the ground-state density matrix $\gamma_{\alpha\beta\sigma} = \langle \Psi | \hat{c}^{\dagger}_{\alpha\sigma} \hat{c}_{\beta\sigma} | \Psi \rangle$ is injective and therefore invertible. The proof is given by contradiction following essentially the same reasoning as Hohenberg and Kohn in the continuum. Let $t_{\alpha\beta}$ and $t'_{\alpha\beta}$ be two different hopping matrices such that the corresponding Hamiltonians $\hat{H} = \sum_{\alpha\beta\sigma} t_{\alpha\beta} \hat{c}^{\dagger}_{\alpha\sigma} \hat{c}_{\beta\sigma} + \hat{W}$ and $\hat{H}' = \sum_{\alpha\beta\sigma} t'_{\alpha\beta} \hat{c}^{\dagger}_{\alpha\sigma} \hat{c}_{\beta\sigma} + \hat{W}$ yield the same ground-state density matrix γ but two different ground states $|\Psi\rangle$ and $|\Psi'\rangle$ (i.e., differing by more than a phase factor). Using that $\hat{H}|\Psi\rangle = E_0|\Psi\rangle$ and $\hat{H}'|\Psi'\rangle = E'_0|\Psi'\rangle$, and applying the variational principle to $\hat{H}$ with $|\Psi'\rangle$ as ansatz wave function, one obtains

$$\begin{aligned} E_0 < \langle \Psi' | \hat{H} | \Psi' \rangle &= \langle \Psi' | \hat{H}' | \Psi' \rangle + \langle \Psi' | \hat{H} - \hat{H}' | \Psi' \rangle \\ &= E'_0 + \sum_{\alpha\beta} (t_{\alpha\beta} - t'_{\alpha\beta}) \sum_{\sigma} \gamma_{\alpha\beta\sigma}. \end{aligned} \tag{7}$$

Notice that the strict inequality is a consequence of the assumed nondegeneracy of the ground state. Interchanging primed and unprimed quantities one obtains

$$E'_0 < E_0 + \sum_{\alpha\beta} (t'_{\alpha\beta} - t_{\alpha\beta}) \sum_{\sigma} \gamma_{\alpha\beta\sigma}. \tag{8}$$

Finally, the addition of the inequalities (7) and (8) yields the contradiction $E_0 + E_0' < E_0 + E_0'$, which completes the proof.

As a consequence of the invertibility of the mapping between the ground state $|\Psi\rangle$ and the ground-state density matrix γ, we can regard $|\Psi\rangle = |\Psi[\gamma]\rangle$ as a functional of γ, and therefore all ground-state expectation values of any observable are also functionals of γ. From the previous demonstration it is clear that both the diagonal and the nondiagonal elements of γ need to be taken into account, since the nondiagonal density-matrix elements $\gamma_{\alpha\beta\sigma}$ play a crucial role in deriving the contradiction. In this context it is important to mention that the mapping between the hopping matrix $t_{\alpha\beta}$ and $|\Psi\rangle$ is not injective. In fact one can find hopping matrices $t_{\alpha\beta}$ and $t'_{\alpha\beta}$ yielding the same ground-state $|\Psi\rangle$, even though the operator $\Delta\hat{T} = \sum_{\alpha\beta\sigma}(t_{\alpha\beta} - t'_{\alpha\beta})\hat{c}^\dagger_{\alpha\sigma}c_{\beta\sigma} \neq 0$. In this case $|\Psi\rangle$ is an eigenfunction of the single-particle operator $\Delta\hat{T}$, since $\Delta\hat{T}|\Psi\rangle = (\hat{H} - \hat{H}')|\Psi\rangle = (E_0 - E_0')|\Psi\rangle$. This implies that if the matrices $t_{\alpha\beta}$ and $t'_{\alpha\beta}$ yield the same ground state, they differ only by a single-particle observable which is conserved in the ground state, e.g., $\hat{N}$ or $\hat{S}_z$. For example, adding a magnetic field B to the Hamiltonian in the z direction does not change the ground state $|\Psi\rangle$ for finite-size systems and sufficiently small magnitude B but results in $\Delta\hat{T} \propto \hat{S}_z \neq 0$.

Following the constrained-search formulation of Levy and Lieb, the ground-state energy $E_{\rm gs}$ and the corresponding density matrix $\gamma^{\rm gs}$ are determined by minimizing the energy functional

$$E[\gamma] = T[\gamma] + W[\gamma] \tag{9}$$

with respect to all pure-state N representable density matrices γ.[19] $T[\gamma]$ stands for the single-particle energy functional, which is equal to the average of $\hat{H}_{\rm cond} + \hat{H}_{\rm imp}$ for the given γ, and $W[\gamma]$ is the interaction-energy functional, which represents the lowest possible average of $\hat{W}$ among all states yielding the given γ (see below). In other words, the variational principle for the ground-state density matrix reads $E_{\rm gs} = E[\gamma^{\rm gs}] \leqslant E[\gamma]$ for all γ that derive from a physical N-particle state $|\Psi\rangle$, i.e., for all γ that are given by $\gamma_{\mathbf{k}\mathbf{k}'\sigma} = \langle\Psi|\hat{c}^\dagger_{\mathbf{k}\sigma}\hat{c}_{\mathbf{k}'\sigma}|\Psi\rangle$, $\gamma_{\mathbf{k}f\sigma} = \langle\Psi|\hat{c}^\dagger_{\mathbf{k}\sigma}\hat{f}_\sigma|\Psi\rangle$, and $\gamma_{ff\sigma} = \langle\Psi|\hat{f}^\dagger_\sigma\hat{f}_\sigma|\Psi\rangle$ for some $|\Psi\rangle$. Although an explicit characterization of pure-state N representable density matrices is not known at present, a simple criterion for ensemble N representability is available.[1] By definition, a single-particle density matrix γ is said to be ensemble N representable if a set of pure states $|\Psi_m\rangle$ and weights $w_m \geqslant 0$ exists ($\sum_m w_m = 1$) such that

$$\gamma_{\alpha\beta\sigma} = \sum_m w_m\langle\Psi_m|\hat{c}^\dagger_{\alpha\sigma}\hat{c}_{\beta\sigma}|\Psi_m\rangle, \tag{10}$$

where α and β refer to f or $\mathbf{k}$ states and $\hat{c}^\dagger_{f\sigma}$ stands for $\hat{f}^\dagger_\sigma$. The states $|\Psi_m\rangle$ form a mixed state characterized by the N-particle density matrix $\hat{\Gamma} = \sum_m w_m|\Psi_m\rangle\langle\Psi_m|$ with $\gamma_{\alpha\beta\sigma} = {\rm Tr}\{\hat{\Gamma}\hat{c}^\dagger_{\alpha\sigma}\hat{c}_{\beta\sigma}\}$. Clearly, the pure states $|\Psi_m\rangle$ satisfy the condition $N_e = {\rm Tr}\{\hat{\Gamma}\hat{N}\}$, where $\hat{N}$ denotes the particle number operator. However, they do not have necessarily the same definite number of particles N_e, as in the case of a grand canonical ensemble, for example. One can show that γ is ensemble N representable if and only if all eigenvalues $\eta_{k\sigma}$ of γ satisfy[1,20]

$$0 \leqslant \eta_{k\sigma} \leqslant 1 \quad \text{and} \quad \sum_{k\sigma}\eta_{k\sigma} = N_e. \tag{11}$$

The corresponding single-particle eigenstates $u^k_{i\sigma}$ are called the natural orbitals and $\eta_{k\sigma}$ are the corresponding occupation numbers. Notice that in the framework of the Kohn-Sham scheme of DFT in the continuum the occupation numbers $\eta_{k\sigma}$ are usually taken to be integers because of the assumed noninteracting v-representability of the ground-state density $\rho(\vec{r})$, i.e., the existence of a noninteracting ground state with the same $\rho(\vec{r})$.[1,3] In contrast, LDFT is based on the complete density matrix γ including the off-diagonal elements and yielding the exact correlated kinetic energy. The $\eta_{k\sigma}$ thus refer to the occupation numbers of the natural orbitals in truly correlated states. Except in trivial cases (e.g., $U = 0$) the electronic correlations preclude one from finding a noninteracting ground state with the ground-state density matrix γ. This necessarily implies fractional occupation numbers $\eta_{k\sigma}$.[12,14]

In order to profit from the simple representation (11), we extend the domain of definition in the energy functional (9) to ensemble N representable density matrices γ by following the work of Valone.[21] The first term in Eq. (9), the single-particle energy functional (sometimes denoted as the kinetic-energy functional), is explicitly given by

$$\begin{aligned} T[\gamma] &= {\rm Tr}\{\hat{\Gamma}(\hat{H}_{\rm cond} + \hat{H}_{\rm imp})\} \\ &= \sum_{\mathbf{k}}\varepsilon_{\mathbf{k}}\gamma_{\mathbf{k}\mathbf{k}} + \varepsilon_f\gamma_{ff} + \sum_{\mathbf{k}}V_{\mathbf{k}f}(\gamma_{\mathbf{k}f} + \gamma_{f\mathbf{k}}), \end{aligned} \tag{12}$$

where $\gamma_{\alpha\beta} = \gamma_{\alpha\beta\uparrow} + \gamma_{\alpha\beta\downarrow}$ and $\gamma_{\alpha\beta\sigma} = {\rm Tr}\{\hat{\Gamma}\hat{c}^\dagger_{\alpha\sigma}\hat{c}_{\beta\sigma}\}$. It is a central feature of LDFT that the kinetic energy T is given exactly. The second term in Eq. (9), the interaction-energy functional, is given by the constrained search

$$\begin{aligned} W[\gamma] &= \min_{\hat{\Gamma}\to\gamma}{\rm Tr}\{\hat{\Gamma}\hat{W}\} \\ &= \min_{\hat{\Gamma}\to\gamma}U\sum_m w_m\langle\Psi_m|\hat{n}_{f\uparrow}\hat{n}_{f\downarrow}|\Psi_m\rangle. \end{aligned} \tag{13}$$

Here the minimization runs over all mixed states that satisfy the condition (10) for all α, β, and σ. Consequently, $W[\gamma]$ represents the minimum of the interaction energy (i.e., minimum number of double occupations on the f orbital for $U > 0$) that is compatible with a given density matrix γ, i.e., with a given charge distribution and degree of electron delocalization. W depends linearly on the interaction parameter U very much as the interaction-energy functional in Hohenberg-Kohn theory depends linearly on e^2.[1] Notice that $W[\gamma]$ is independent of the system under study, i.e., independent of the parameters $\varepsilon_{\mathbf{k}}$, ε_f, and $V_{\mathbf{k}f}$. In this sense, W constitutes a universal functional of γ. However, $W[\gamma]$ depends on the kind of the many-particle interactions (in the present case local), on the number of particles $N_e = {\rm Tr}\{\gamma\}$ corresponding to the given γ, and on the structure of the many-body Hilbert space as defined by N_e and the number of atoms N_a.

Valone demonstrated that the extension to ensemble N representable density matrices γ does not change the physics of the obtained results.[21] Indeed, assuming that the ground state is nondegenerate and using both the variational principle

and the convexity of the ground-state energy $E_{\rm gs}(N_e)$ as a function of N_e [i.e., $\partial E_{\rm gs}/\partial N_e\,(N_e+1) > \partial E_{\rm gs}/\partial N_e\,(N_e)$] two main properties can be shown.[22] First, the minimization of $E[\gamma]$ with respect to ensemble N representable γ yields a pure-state N representable γ, namely the density matrix $\gamma^{\rm gs}$ corresponding to the ground state. And second, for any ground-state representable γ the minimization on the right-hand side of Eq. (13) is equivalent to a minimization within the subset of pure states (i.e., $w_{m'} = \delta_{m'm}$ for some m). Let us recall that γ is said to be ground-state representable or v representable if it can be derived from the ground state of the Hamiltonian (1) for some set of parameters $\varepsilon_{\mathbf{k}}$, ε_f, $V_{\mathbf{k}f}$, and U. These density matrices are the physically relevant ones. Consequently, Eq. (13) is a proper extension of the interaction-energy functional $W[\gamma]$ to ensemble N representable γ. Although the explicit form of the exact interaction-energy functional $W[\gamma]$ is unknown, it is possible to determine some important properties by studying relevant limits, symmetries, and invariances.

III. PROPERTIES OF THE INTERACTION-ENERGY FUNCTIONAL

In the following we discuss some exact properties of the interaction-energy functional of the Anderson model, which are important for the derivation of accurate approximations.

(1) *Uncorrelated limit.* The ensemble N representability of γ imposes constraints on the degree of charge fluctuations $\gamma_{\mathbf{k}f\sigma}$ between the f orbital and the conduction-band states. Let us recall that both γ and $1-\gamma$ are positive definite matrices, since the eigenvalues $\eta_{k\sigma}$ of the single-particle density matrix satisfy $0 \leqslant \eta_{k\sigma} \leqslant 1$. This implies that for any given occupation of the f and $\mathbf{k}$ orbitals $\gamma_{ff\sigma}$ and $\gamma_{\mathbf{kk}\sigma}$, the off-diagonal element $\gamma_{\mathbf{k}f\sigma}$ is bounded by[23]

$$|\gamma_{\mathbf{k}f\sigma}| \leqslant \sqrt{\gamma_{ff\sigma}\gamma_{\mathbf{kk}\sigma}} \tag{14}$$

and

$$|\gamma_{\mathbf{k}f\sigma}| \leqslant \sqrt{(1-\gamma_{ff\sigma})(1-\gamma_{\mathbf{kk}\sigma})}. \tag{15}$$

In the uncorrelated limit ($U=0$) the occupations $\eta_{k\sigma}$ (of natural orbitals) are 0 or 1. Therefore, in the special case of an uncorrelated two-level system the ground-state density matrix $\gamma^0_{\mathbf{k}f\sigma}$ coincides with these general bounds:

$$|\gamma^0_{\mathbf{k}f\sigma}| = \begin{cases} \sqrt{\gamma^0_{ff\sigma}\gamma^0_{\mathbf{kk}\sigma}} & \text{if} \quad \gamma^0_{\mathbf{kk}\sigma} + \gamma^0_{ff\sigma} \leqslant 1, \\ \sqrt{\left(1-\gamma^0_{ff\sigma}\right)\left(1-\gamma^0_{\mathbf{kk}\sigma}\right)} & \text{if} \quad \gamma^0_{\mathbf{kk}\sigma} + \gamma^0_{ff\sigma} \geqslant 1. \end{cases} \tag{16}$$

In the following we denote by γ^0 the ground-state density matrix of an arbitrary system having $U=0$. In the absence of degeneracies at the Fermi energy of the single-particle spectrum, the uncorrelated γ^0 is realized by a single Slater determinant. The corresponding interaction energy

$$W[\gamma] \to W_{\rm HF}[\gamma^0] = U\gamma^0_{ff\uparrow}\gamma^0_{ff\downarrow} \tag{17}$$

for $\gamma \to \gamma^0$ is given by the Hartree-Fock theory. From the point of view of LDFT the uncorrelated density matrix γ^0 yields both a maximum of the double occupations $\langle \hat{n}_{f\uparrow}\hat{n}_{f\downarrow}\rangle$ and the lowest single-particle energy T.

The equilibrium condition for the functional derivative of $E[\gamma]$ with respect to $\gamma_{\mathbf{k}f\sigma}$ yields $V_{\mathbf{k}f} + \delta W/\delta\gamma_{\mathbf{k}f\sigma} = 0$ for all ground-state density matrices $\gamma^{\rm gs}$. This holds in particular for the ground-state density matrix γ^0 of any system with vanishing Coulomb repulsion U. Since a noninteracting system is equivalent to a system with fixed Coulomb repulsion U and $|V_{\mathbf{k}f}| \to \infty$, we conclude $\delta W/\delta\gamma_{\mathbf{k}f\sigma} \to \infty$ for $\gamma \to \gamma^0$. A similar argument shows that $\delta W/\delta\gamma_{ff\sigma} \to \infty$ for $\gamma \to \gamma^0$. This implies that an arbitrary small value of $U \neq 0$ results in a nonvanishing change in $\gamma^{\rm gs}$ with respect to γ^0, as expected from perturbation theory.

(2) *Strongly correlated limit.* This case corresponds to the minimum of $\langle \hat{n}_{f\uparrow}\hat{n}_{f\downarrow}\rangle$ for the given charge distribution $\gamma_{\mathbf{kk}\sigma}$ and $\gamma_{ff\sigma}$. Consequently, one has[24]

$$W[\gamma] \to W_\infty[\gamma^\infty] = U\max\left\{0, \gamma^\infty_{ff} - 1\right\} \tag{18}$$

for $\gamma_{\mathbf{k}f\sigma} \to \gamma^\infty_{\mathbf{k}f\sigma}$, where $\gamma^\infty_{\mathbf{k}f\sigma}$ derives from a strongly correlated N-particle state yielding the maximum degree of charge fluctuations under the constraint of minimum $\langle \hat{n}_{f\uparrow}\hat{n}_{f\downarrow}\rangle$. Notice that $\gamma^\infty_{\mathbf{k}f\sigma}$ depends on the values of $\gamma_{\mathbf{kk}\sigma}$ and $\gamma_{ff\sigma}$. Moreover, $|\gamma^\infty_{\mathbf{k}f\sigma}| \leqslant |\gamma^0_{\mathbf{k}f\sigma}|$, since decreasing $\langle \hat{n}_{f\uparrow}\hat{n}_{f\downarrow}\rangle$ can only be achieved by decreasing the degree of charge fluctuations. Consequently, $\gamma^\infty_{\mathbf{k}f\sigma}$ corresponds to the ground state of a system with Coulomb repulsion $U \to \infty$. In contrast to the uncorrelated limit, determining $\gamma^\infty_{\mathbf{k}f\sigma}$ is far from trivial. Therefore, its value can be a source of inaccuracy in LDFT calculations for very large U.

(3) *Electron-hole symmetry.* Since the annihilation of an electron is equivalent to the creation of a hole, one can introduce the electron-hole transformation $\hat{h}^\dagger_{i\sigma} = \hat{c}_{i\sigma}$ and $\hat{h}_{i\sigma} = \hat{c}^\dagger_{i\sigma}$. Thus, the single-particle density matrix transforms according to $\gamma_{ij\sigma} = \langle\Psi|\delta_{ij} - \hat{h}^\dagger_{j\sigma}h_{i\sigma}|\Psi\rangle = \delta_{ij} - \gamma^h_{ji\sigma}$, and the interaction-energy functional satisfies

$$W[\gamma] = W[\gamma^h] + U\left(1-\gamma^h_{ff}\right). \tag{19}$$

Any sound approximation to $W[\gamma]$ should fulfill this condition.

(4) *Unitary transformations within the conduction band.* The interaction-energy functional $W[\gamma]$ is invariant under unitary transformations among the orbitals in the conduction band. In order to show this explicitly consider a unitary matrix $S_{\mathbf{kk}'\sigma}$ and let $\hat{S}_\sigma$ be the associated unitary operator which acts on each creation operator in the N-particle Hilbert space. $\hat{S}_\sigma$ is defined by the transformation

$$\hat{c}^\dagger_{\mathbf{k}\sigma} \to \sum_{\mathbf{k}'} S_{\mathbf{kk}'\sigma}\hat{c}^\dagger_{\mathbf{k}'\sigma} \quad \text{for all } \mathbf{k} \quad \text{and} \quad \hat{f}^\dagger_\sigma \to \hat{f}^\dagger_\sigma. \tag{20}$$

For any N-particle state $|\Psi\rangle$ with density matrix $\gamma_{\mathbf{kk}'\sigma} = \langle\Psi|\hat{c}^\dagger_{\mathbf{k}\sigma}\hat{c}_{\mathbf{k}'\sigma}|\Psi\rangle$, the transformed single-particle density matrix with respect to $\hat{S}_\sigma$ is given by

$$\tilde{\gamma}_{\mathbf{kk}'\sigma} = \langle\Psi|\hat{S}^\dagger_\sigma\hat{c}^\dagger_{\mathbf{k}\sigma}\hat{c}_{\mathbf{k}'\sigma}\hat{S}_\sigma|\Psi\rangle = \sum_{\mathbf{k}_1\mathbf{k}_2} S^*_{\mathbf{k}_2\mathbf{k}\sigma}\gamma_{\mathbf{k}_2\mathbf{k}_1\sigma}S_{\mathbf{k}_1\mathbf{k}'\sigma}, \tag{21}$$

where $\gamma_{\mathbf{kk}'\sigma}$ ($\tilde{\gamma}_{\mathbf{kk}'\sigma}$) denotes the density matrix $\gamma_{\alpha\beta\sigma}$ ($\tilde{\gamma}_{\alpha\beta\sigma}$) restricted to the subspace which is spanned by the conduction-band orbitals. In other words, $\hat{S}_\sigma$ represents a bijective mapping from the state $|\Psi\rangle$ with density matrix $\gamma_{\mathbf{kk}'\sigma}$ onto the state $\hat{S}_\sigma|\Psi\rangle$ with the density matrix $\tilde{\gamma}_{\mathbf{kk}'\sigma}$ given by Eq. (21).

Since $\hat{S}_\sigma$ and $\hat{n}_{f\sigma}$ commute, we have $\langle\Psi|\hat{S}_\sigma^\dagger \hat{n}_{f\uparrow}\hat{n}_{f\downarrow}\hat{S}_\sigma|\Psi\rangle = \langle\Psi|\hat{n}_{f\uparrow}\hat{n}_{f\downarrow}|\Psi\rangle$ for arbitrary $|\Psi\rangle$. Consequently, $W[\gamma] = W[\tilde{\gamma}]$.

In the following section we derive an approximation to the interaction-energy functional $W[\gamma]$ by taking advantage of these general properties.

IV. TWO-LEVEL APPROXIMATION

A. Motivation and background

The invariance of $W[\gamma]$ under unitary transformations within the conduction band allows one to simplify the interaction-energy functional, since it is always possible to find a basis transformation $\hat{S}_\sigma$ such that the impurity orbital experiences direct charge fluctuations to only one particular conduction-band state $\hat{c}_{s\sigma}^\dagger$. In analogy to Eqs. (20) and (21) we have $\tilde{\gamma}_{\mathbf{k}f\sigma} = \langle\Psi|\hat{S}_\sigma^\dagger \hat{c}_{\mathbf{k}\sigma}^\dagger \hat{f}_\sigma \hat{S}_\sigma|\Psi\rangle = \sum_{\mathbf{k}'} S_{\mathbf{k}'\mathbf{k}\sigma}^* \gamma_{\mathbf{k}'f\sigma}$. The unitary transformation we are looking for is given by $S_{\mathbf{k}s\sigma} = \gamma_{\mathbf{k}f\sigma}/\Gamma_{sf\sigma}$, where

$$\Gamma_{sf\sigma} = \sqrt{\sum_{\mathbf{k}} |\gamma_{\mathbf{k}f\sigma}|^2} \tag{22}$$

represents the effective degree of fluctuations. Thus, the transformed single-particle density matrix $\tilde{\gamma}$ takes the desired form

$$\tilde{\gamma}_\sigma = \begin{pmatrix} * & \cdots & * & * & 0 \\ \vdots & \ddots & \vdots & \vdots & \vdots \\ * & \cdots & * & * & 0 \\ * & \cdots & * & \tilde{\gamma}_{ss\sigma} & \Gamma_{sf\sigma} \\ 0 & \cdots & 0 & \Gamma_{sf\sigma}^* & \gamma_{ff\sigma} \end{pmatrix}, \tag{23}$$

where

$$\tilde{\gamma}_{ss\sigma} = \frac{1}{\Gamma_{sf\sigma}^2} \sum_{\mathbf{k_1}\mathbf{k_2}} \gamma_{\mathbf{k_1}\mathbf{f}\sigma}^* \gamma_{\mathbf{k_1}\mathbf{k_2}\sigma} \gamma_{\mathbf{k_2}\mathbf{f}\sigma} \tag{24}$$

and the star entries (*) denote elements that are in general different from zero. In spite of the fact that an electron at the localized impurity orbital fluctuates only to the particular single-particle state $\hat{c}_{s\sigma}^\dagger$, it is important to remark that there are still fluctuations $\gamma_{\mathbf{k}s\sigma}$ between this orbital and the rest of the conduction band. In other words, $\hat{c}_{s\sigma}^\dagger$ does not usually correspond to a conduction-band eigenstate.

Motivated by the possibility to transform the density matrix γ into the form (23) and by the invariance of W under unitary transformations within the conduction band, we propose to approximate the interaction-energy functional $W[\gamma]$ by the interaction energy of an effective two-level (2L) problem having the density matrix

$$\gamma_\sigma^{2\mathrm{L}} = \begin{pmatrix} \tilde{\gamma}_{ss\sigma} & \Gamma_{sf\sigma} \\ \Gamma_{sf\sigma}^* & \gamma_{ff\sigma} \end{pmatrix}. \tag{25}$$

For the purpose of deriving the functional dependence of $W[\gamma]$ we assume that the two-level block (25) can be decoupled from the rest of the conduction band. The *two-level approximation* (TLA) then reads

$$W^{2\mathrm{L}}[\gamma] = W^{2\mathrm{L}}[\gamma^{2\mathrm{L}}], \tag{26}$$

where $\gamma^{2\mathrm{L}}$ is given by Eq. (25), and the matrix elements $\Gamma_{sf\sigma}$ and $\tilde{\gamma}_{ss\sigma}$ are given by (22) and (24). It should be however noted that it is in general not possible to completely decouple the density matrix into a two-level block consisting of the localized impurity orbital $\hat{f}_\sigma^\dagger$ and $\hat{c}_{s\sigma}^\dagger$, and another block containing the rest of the conduction-band states. Only in special cases, for example, when the density matrix γ is derived from N-particle states with particular symmetries, can one show that such a decoupling is rigorous. In the following sections we discuss a number of applications showing that the simple two-level ansatz is indeed a good approximation.

B. Exact limits of $W^{2\mathrm{L}}$

Before the actual applications, it is useful to demonstrate that the TLA is exact in some relevant limiting cases. First of all, in the uncorrelated limit ($U = 0$) the functional $E[\gamma]$ is exact, since the kinetic-energy functional $T[\gamma]$ is exact and $W[\gamma]$ vanishes [see Eq. (12)]. Notice that this need not imply that the functional dependence of $W/U = \langle\hat{n}_{f\uparrow}\hat{n}_{f\downarrow}\rangle$ is accurately given. Nevertheless, as we shall see in Sec. V A, the number of f-level double occupations $\langle\hat{n}_{f\uparrow}\hat{n}_{f\downarrow}\rangle$ is very well reproduced by the TLA. Besides the noninteracting limit, the TLA is exact in the limit of a totally degenerate conduction band and the limit of widely separated discrete conduction-band levels. These facts underpin the assumption that the particular single-particle orbital $\hat{c}_{s\sigma}^\dagger$ can be decoupled from the rest of the conduction band for the purpose of computing the interaction-energy functional $W[\gamma]$.

(1) *Vanishing conduction band width.* This case corresponds, without loss of generality, to $\varepsilon_{\mathbf{k}} = 0$ for all $\mathbf{k}$. In order to demonstrate the exactness of the TLA we determine the ground-state density matrix γ^{gs}. To this aim we apply a unitary transformation $\hat{S}'_\sigma$ within the conduction band so that $\hat{b}_{s\sigma}^\dagger = \sum_{\mathbf{k}} V_{\mathbf{k}f}\hat{c}_{\mathbf{k}\sigma}^\dagger/\sqrt{\sum_{\mathbf{k}'}|V_{\mathbf{k}'f}|^2}$ [see (20)]. The Hamiltonian (1) can then be written as

$$\hat{H} = \sum_\sigma \varepsilon_f \hat{n}_{f\sigma} + \sqrt{\sum_{\mathbf{k}} |V_{\mathbf{k}f}|^2} \cdot \sum_\sigma (\hat{b}_{s\sigma}^\dagger \hat{f}_\sigma + \hat{f}_\sigma^\dagger \hat{b}_{s\sigma}) + U\hat{n}_{f\uparrow}\hat{n}_{f\downarrow}. \tag{27}$$

Therefore, the subspace spanned by $\hat{f}_\sigma^\dagger$ and $\hat{b}_{s\sigma}^\dagger$ is decoupled from the rest of the conduction states. Since $\hat{H}$ describes an effective two-level problem, the corresponding ground-state density matrix γ^{gs} (after application of $\hat{S}'_\sigma$) takes the form

$$\tilde{\gamma}_\sigma^{\mathrm{gs}} = \begin{pmatrix} * & 0 & \cdots & 0 & 0 \\ 0 & \ddots & \ddots & \vdots & \vdots \\ \vdots & \ddots & * & 0 & 0 \\ 0 & \cdots & 0 & \tilde{\gamma}_{ss\sigma} & \Gamma_{sf\sigma} \\ 0 & \cdots & 0 & \Gamma_{sf\sigma}^* & \gamma_{ff\sigma} \end{pmatrix}, \tag{28}$$

where the two-level block (25) is decoupled from the rest of the conduction band.[25] Consequently, the TLA is exact for a totally degenerate conduction band. Although the conduction band is large in simple and noble metals, one may argue that the main electronic charge fluctuations between impurity and conduction band occur in a relatively narrow energy range

around the Fermi energy ε_F. It is therefore reasonable to expect that the TLA is a sound approach in realistic cases.

(2) *Widely separated discrete conduction-band levels.* This limit corresponds to large hopping integrals t, for which the dominant term in the Hamiltonian (1) is the single-particle contribution of the conduction band $\hat{H}_{\rm cond}$. Since the remaining terms $\hat{H}_{\rm imp}+\hat{W}$ are small compared to $\hat{H}_{\rm cond}$, i.e., $|V_{sf}|\ll t$, $|\varepsilon_f-\varepsilon_i^s|\ll t$, and $U\ll t$, it is reasonable to take into account the operator $\hat{H}_{\rm imp}+\hat{W}$ as a perturbation.[26] Therefore, in zeroth order the ground state is a single Slater determinant $|\Psi^0\rangle$ with single-particle states filled up to the Fermi level ε_F. In the case of degenerate ground states $|\Psi_j^0\rangle$, one considers the normalized linear combination $|\Psi^0\rangle=\sum_j\alpha_j|\Psi_j^0\rangle$ which minimizes the expectation value $\langle\hat{H}_{\rm imp}+\hat{W}\rangle$. Let ε_{LUCO} denote the energy of the lowest unoccupied conduction-band orbital (LUCO) in $|\Psi^0\rangle$. Taking into account the hybridization energy $V_{\mathbf{k}f}$ between the impurity orbital and the conduction band, the contribution to the ground state of states $|\Psi'\rangle$ with $\hat{n}_{\rm LUCO}|\Psi'\rangle=|\Psi'\rangle$ can be estimated in first-order perturbation theory as

$$\frac{\langle\Psi'|\hat{H}_{\rm imp}+\hat{W}|\Psi^0\rangle}{\varepsilon_f-\varepsilon_{LUCO}}=\frac{\langle\Psi'|\hat{H}_{\rm imp}|\Psi^0\rangle}{\varepsilon_f-\varepsilon_{LUCO}}\simeq\frac{|V_{sf}|}{\Delta},\tag{29}$$

where Δ is the average single-particle energy difference between adjacent conduction-band states. This corresponds to a charge fluctuation from the f orbital to the LUCO. Notice that the interaction-energy operator $\hat{W}$ does not change the occupation of the conduction-band states and therefore does not contribute to the first-order correction of the occupation of the LUCO. Since Δ scales linearly with t and $|V_{sf}|\ll t$, one obtains $\langle\hat{n}_{\rm LUCO}\rangle\simeq|V_{sf}|^2/\Delta^2\to 0$ for $t\to\infty$. A similar argument yields $\gamma_{\mathbf{k}\mathbf{k}\sigma}\simeq|V_{sf}|^2/\Delta^2\to 0$ for $t\to\infty$ for all conduction-band states above the LUCO. Using the electron-hole symmetry, one also obtains $1-\gamma_{\mathbf{k}\mathbf{k}\sigma}\simeq|V_{sf}|^2/\Delta^2\to 0$ for $t\to\infty$ for all doubly occupied conduction-band orbitals below the Fermi level ε_F. Consequently, in the limit of widely separated discrete conduction-band levels, there is only one relevant conduction-band state, namely the lowest partially occupied orbital at ε_F. This orbital and the localized impurity state $\hat{f}_\sigma^\dagger$ define a two-level problem which dominates the low-energy physics. Consequently, the TLA is perfectly accurate.

Since the TLA is exact in the limits of very narrow and very wide level separation at ε_F, it is reasonable to expect that it will provide accurate results in the intermediate region as well. Moreover, the universality of $W[\gamma]$, i.e., the fact that one single functional $W[\gamma]$ describes the interaction energy for all lattice structures and single-particle parameters $\varepsilon_{\mathbf{k}}$, ε_f, and $V_{\mathbf{k}f}$, encourages the development of simple transparent approximations in the same spirit as the local approximation to DFT in the continuum. In the following we develop a universally applicable approximation to $W[\gamma]$ on the basis of the exact solution of the two-level problem.

C. Interaction-energy functional

The purpose of this section is to derive the analytical expression for the interaction-energy functional $W^{\rm 2L}[\gamma]$ in a two-level system consisting of the localized impurity orbital f and one delocalized orbital s. In this reduced subspace the Anderson model reads

$$\hat{H}^{\rm 2L}=\sum_\sigma[\varepsilon_f\hat{n}_{f\sigma}+V_{sf}(\hat{c}_{s\sigma}^\dagger\hat{f}_\sigma+\hat{f}_\sigma^\dagger\hat{c}_{s\sigma})]+U\hat{n}_{f\uparrow}\hat{n}_{f\downarrow}.\tag{30}$$

First of all we consider an integer number of electrons $N_e=\gamma_{ss}+\gamma_{ff}$ and in particular the nontrivial half-filled case $N_e=2$. For simplicity, the hybridization parameter V_{sf} is assumed to be real and positive.[27] Consequently, the eigenstates of Eq. (30) and the ground-state representable density matrices γ are real as well. Taking into account that the ground state of the many-body Anderson model is a singlet,[28] we focus on states which satisfy $\gamma_{ij\uparrow}=\gamma_{ij\downarrow}$ for all sites ij. In this case the interaction-energy functional is given by

$$W^{\rm 2L}(\gamma_{ff},\gamma_{sf})=\min_{\substack{\hat{\Gamma}\to\gamma\\ \text{singlet}}}U\sum_m w_m\langle\Psi_m|\hat{n}_{f\uparrow}\hat{n}_{f\downarrow}|\Psi_m\rangle,\tag{31}$$

where the minimization runs over all mixed singlet states that yield the single-particle density matrix γ. The normalized singlet states $|\Psi_m\rangle$ can be written as a linear combination of $\hat{c}_{s\uparrow}^\dagger\hat{c}_{s\downarrow}^\dagger|{\rm vac}\rangle$, $\hat{f}_\uparrow^\dagger\hat{f}_\downarrow^\dagger|{\rm vac}\rangle$, and $1/\sqrt{2}(\hat{f}_\uparrow^\dagger\hat{c}_{s\downarrow}^\dagger-\hat{f}_\downarrow^\dagger\hat{c}_{s\uparrow}^\dagger)|{\rm vac}\rangle$. A straightforward, however somewhat lengthy, calculation given in the Appendix yields

$$W^{\rm 2L}(\gamma_{ff},\gamma_{sf})=\begin{cases}U\left(\dfrac{\gamma_{ff}}{2}-\dfrac{|\gamma_{sf}|^2/4}{1-\sqrt{|\gamma_{sf}^0|^2-|\gamma_{sf}|^2}}\right) & \text{if}\quad |\gamma_{sf}|>\gamma_{sf}^\infty,\\ W_\infty(\gamma_{ff}) & \text{if}\quad |\gamma_{sf}|\leqslant\gamma_{sf}^\infty.\end{cases}\tag{32}$$

Comparison with the constraint (16) gives $\gamma_{sf}^0=\sqrt{\gamma_{ff}(2-\gamma_{ff})}$ for the maximum degree of charge fluctuations. The corresponding interaction energy $W^{\rm 2L}(\gamma_{ff},\gamma_{sf}^0)$ coincides with the Hartree-Fock energy $W_{\rm HF}=U\gamma_{ff}^2/4$ [see Eq. (32)]. In the strongly correlated limit we have

$$\gamma_{sf}^\infty=\begin{cases}\sqrt{2\gamma_{ff}(1-\gamma_{ff})} & \text{if}\quad \gamma_{ff}\leqslant 1,\\ \sqrt{2(2-\gamma_{ff})(\gamma_{ff}-1)} & \text{if}\quad \gamma_{ff}>1,\end{cases}\tag{33}$$

and

$$W_\infty(\gamma_{ff})=\begin{cases}0 & \text{if}\quad \gamma_{ff}\leqslant 1,\\ U(\gamma_{ff}-1) & \text{if}\quad \gamma_{ff}>1,\end{cases}\tag{34}$$

which coincides with Eq. (18). A derivation of Eqs. (33) and (34) is given in the Appendix.

Figure 1 shows $W^{\rm 2L}$, given by Eq. (32), as a function of γ_{sf} for different f-level occupations γ_{ff}. One can easily recognize some of the general properties mentioned in Sec. III. In the uncorrelated limit the maximum degree of charge fluctuations $|\gamma_{sf}|=\gamma_{sf}^0$ entails the maximum $\langle\hat{n}_{f\uparrow}\hat{n}_{f\downarrow}\rangle$ and the interaction energy is given by $W_{\rm HF}=U\gamma_{ff}^2/4$. Moreover, the functional derivative $\delta W^{\rm 2L}/\delta\gamma_{sf}$ has the correct divergency for $|\gamma_{sf}|\to\gamma_{sf}^0$. As $|\gamma_{sf}|$ decreases, it is possible to find states with reduced double occupations $\langle\hat{n}_{f\uparrow}\hat{n}_{f\downarrow}\rangle$ and thus $W^{\rm 2L}$ decreases. The strongly correlated limit is characterized

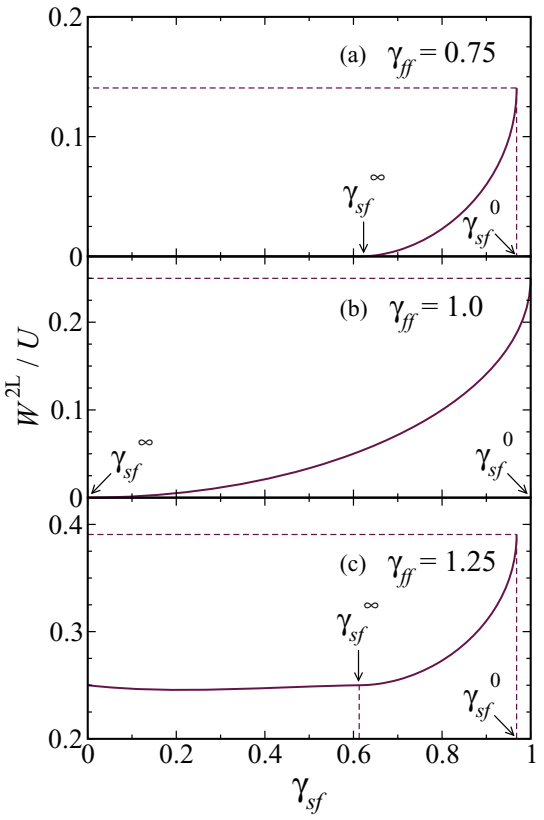

FIG. 1. (Color online) Two-level singlet interaction-energy functional W^{2L} of the half-filled Anderson model as a function of the off-diagonal density matrix element γ_{sf}. Results are given for (a) $\gamma_{ff} = 0.75$, (b) $\gamma_{ff} = 1.0$, and (c) $\gamma_{ff} = 1.25$. γ_{sf}^{∞} refers to the limit of strong correlations and γ_{sf}^{0} to the uncorrelated limit. Notice that W^{2L} is also defined for $\gamma_{sf} < 0$ and that it depends only on $|\gamma_{sf}|$.

by the minimal $\langle \hat{n}_{f\uparrow}\hat{n}_{f\downarrow}\rangle$ and by $|\gamma_{sf}| = \gamma_{sf}^{\infty}$. Concerning intermediate values let us recall that the single-particle energy $T = \varepsilon_f \gamma_{ff} + V_{sf}(\gamma_{sf} + \gamma_{fs})$ increases monotonously from the uncorrelated to the strongly correlated limit ($T < 0$). Therefore, for any finite Coulomb repulsion U, the ground-state density matrix $\gamma^{\rm gs}$ results from a competition between lowering T by increasing $|\gamma_{sf}|$ and lowering the Coulomb energy by decreasing $|\gamma_{sf}|$. Consequently, only the density matrices γ satisfying $\gamma_{sf}^{\infty} \leqslant |\gamma_{sf}| \leqslant \gamma_{sf}^{0}$ can be derived from the ground states of the Anderson Hamiltonian (30) for some parameters ε_f, V_{sf}, and U. These γ are therefore ground-state representable (pure-state v representable). In contrast, density matrices satisfying $|\gamma_{sf}| < \gamma_{sf}^{\infty}$ are not pure-state v representable, although they can be derived from a pure state. Fig. 2 illustrates the domains of ground-state, pure-state, and ensemble representability of γ for the half-filled two-level system.

So far, we have considered only an integer particle number $N_e = \gamma_{ss} + \gamma_{ff} = 2$. This is valid because $[\hat{N}^{2L}, \hat{H}^{2L}] = 0$, where $\hat{N}^{2L} = \sum_\sigma (\hat{f}_\sigma^\dagger \hat{f}_\sigma + \hat{c}_{s\sigma}^\dagger \hat{c}_{s\sigma})$ measures the number of electrons in the localized impurity orbital and in the particular conduction-band orbital. However, in systems with more than one delocalized orbital, $\hat{N}^{2L}$ is no longer conserved. Physically, this means that charge fluctuations between conduction-

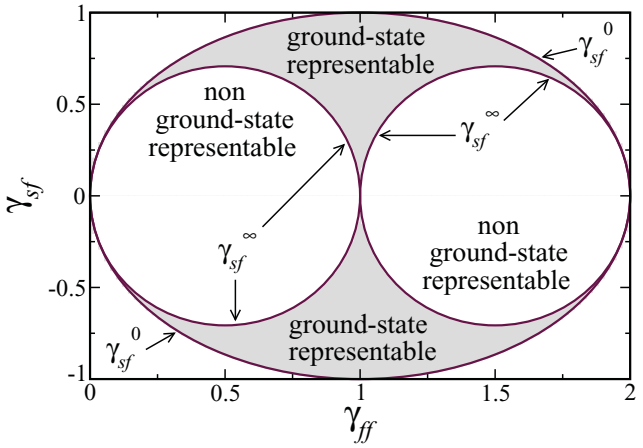

FIG. 2. (Color online) Domain of representability of the single-particle density matrix γ for the half-filled two-level problem (singlet subspace) in terms of the occupation of the localized impurity orbital γ_{ff} and the degree of charge fluctuations γ_{sf}. Only the density matrices γ satisfying $\gamma_{sf}^{\infty} \leqslant |\gamma_{sf}| \leqslant \gamma_{sf}^{0}$ are ground-state representable (pure-state v representable). The domains of pure-state and ensemble N representability coincide and are simply given by $|\gamma_{sf}| \leqslant \gamma_{sf}^{0}$.

band orbitals couple the impurity level with the rest of the conduction band. We must therefore extend the two-level interaction-energy functional to fractional particle numbers $N_e \in [0,4]$.

Given a density matrix γ with $0 \leqslant N_e = \gamma_{ff} + \gamma_{ss} \leqslant 2$ in the two-level subspace, we consider mixed states $\hat{\Gamma}$ of the form

$$\hat{\Gamma} = \sum_{m'} w_{m'} |\Psi_{m'}\rangle\langle\Psi_{m'}| \tag{35}$$

having $\sum_{m'} w_{m'} = 1$ and satisfying the constraint

$$\gamma_{\alpha\beta} = \mathrm{Tr}\left\{\hat{\Gamma} \sum_\sigma \hat{c}_{\alpha\sigma}^\dagger \hat{c}_{\beta\sigma}\right\}. \tag{36}$$

In the singlet subspace, the $\hat{\Gamma}$ that minimizes the interaction energy under the constraint (36) reads

$$\hat{\Gamma} = \frac{N_e}{2}\hat{\Gamma}^{(2)} + \left(1 - \frac{N_e}{2}\right)|\mathrm{vac}\rangle\langle\mathrm{vac}|, \tag{37}$$

where $\hat{\Gamma}^{(2)} = \sum_m w_m |\Psi_m^{(2)}\rangle\langle\Psi_m^{(2)}|$ is the superposition of two-particle singlet states $|\Psi_m^{(2)}\rangle$ and $|\mathrm{vac}\rangle$ stands for the empty two-level state. Using this ansatz and the electron-hole symmetry (19) one obtains the explicit two-level interaction-energy functional, as described in the Appendix. The final result reads

$$W^{2L}(\gamma_{ff},\gamma_{ss},\gamma_{sf})/U = \frac{\gamma_{ff}}{2} - \frac{|\gamma_{sf}|^2/4}{\min\left\{\frac{N_e}{2}, 2 - \frac{N_e}{2}\right\} - \sqrt{|\gamma_{sf}^0|^2 - |\gamma_{sf}|^2}} \tag{38}$$

for $|\gamma_{sf}| > \gamma_{sf}^{\infty}$ and $W^{2L}(\gamma_{ff},\gamma_{ss},\gamma_{sf}) = W_\infty(\gamma_{ff},\gamma_{ss})$ for $|\gamma_{sf}| \leqslant \gamma_{sf}^{\infty}$. According to the constraint (16), the maximum degree of charge fluctuations is given by

$$\gamma_{sf}^0 = 2\gamma_{sf\sigma}^0 = \begin{cases} \sqrt{\gamma_{ss}\gamma_{ff}} & \text{if} \quad N_e \leqslant 2, \\ \sqrt{(2-\gamma_{ff})(2-\gamma_{ss})} & \text{if} \quad N_e > 2, \end{cases} \tag{39}$$

while in the strongly correlated limit we have

$$\gamma_{sf}^{\infty} = \begin{cases} \sqrt{2\gamma_{ff}\left(\frac{N_e}{2} - \gamma_{ff}\right)} & \text{if } N_e \leqslant 2,\ \gamma_{ff} \leqslant \frac{N_e}{2}, \\ \sqrt{2\gamma_{ss}\left(\gamma_{ff} - \frac{N_e}{2}\right)} & \text{if } N_e \leqslant 2,\ \gamma_{ff} > \frac{N_e}{2}, \\ \sqrt{2\left(2-\gamma_{ff}\right)\left(\gamma_{ff} - \frac{N_e}{2}\right)} & \text{if } N_e > 2,\ \gamma_{ff} > \frac{N_e}{2}, \\ \sqrt{2\left(2-\gamma_{ss}\right)\left(\frac{N_e}{2} - \gamma_{ff}\right)} & \text{if } N_e > 2,\ \gamma_{ff} \leqslant \frac{N_e}{2}, \end{cases} \tag{40}$$

and

$$W_{\infty}(\gamma_{ff},\gamma_{ss}) = \begin{cases} 0 & \text{if } N_e \leqslant 2, \gamma_{ff} \leqslant \frac{N_e}{2}, \\ U(\gamma_{ff} - N_e/2) & \text{if } N_e \leqslant 2, \gamma_{ff} > \frac{N_e}{2}, \\ U(\gamma_{ff} - 1) & \text{if } N_e > 2, \gamma_{ff} > \frac{N_e}{2}, \\ U(N_e/2 - 1) & \text{if } N_e > 2, \gamma_{ff} \leqslant \frac{N_e}{2}. \end{cases} \tag{41}$$

It is important to remark that the functional defined in Eqs. (38)–(41) is exact only for $N_e = 2$. For particle numbers $N_e < 2\,(N_e > 2)$, the present approximation $W^{2L}(\gamma_{ff},\gamma_{ss},\gamma_{sf})$ is derived from states which can be written as a linear combination of pure singlet states with definite particle numbers $N_e = 2$ and $N_e = 0\,(N_e = 4)$. Therefore W^{2L} is not applicable to spin-polarized systems with odd particle numbers ($N_e = 1$ or 3). Concerning singlet states one expects $N_e^{2L} \simeq 2$, even in realistic systems with an arbitrary number of levels, since having one electron per orbital ($N_e^{2L} = 2$) optimizes the degree of charge fluctuations $\gamma_{\mathbf{k}f}$. Therefore, the approximation W^{2L} should remain accurate in widespread applications.

Finally, for the applications we take advantage of the invariance of W under unitary transformations within the conduction band and approximate the interaction-energy functional $W[\gamma]$ for arbitrary systems by the two-level functional $W^{2L}(\gamma_{ff},\tilde{\gamma}_{ss},\Gamma_{sf})$, where the matrix elements Γ_{sf} and $\tilde{\gamma}_{ss}$ are given by (22) and (24).

V. APPLICATIONS TO FINITE RINGS

Given an explicit approximation $W^{2L}(\gamma)$ to the interaction-energy functional [Eqs. (38)–(41)] and using the exact expression for the single-particle energy functional $T[\gamma]$ [Eq. (12)], we minimize the total-energy functional

$$E[\gamma] = T[\gamma] + W^{2L}[\gamma] \tag{42}$$

with respect to γ in order to obtain the ground-state density matrix γ^{gs} and the electronic ground-state properties that are functionals of γ, e.g., the kinetic, interaction, and total energy, as well as the average occupation γ_{ff} of the impurity orbital. The numerical minimization procedure is based on the representation of $\gamma_{\alpha\beta\sigma} = \sum_k u_{\alpha\sigma}^k \eta_{k\sigma} (u_{\beta\sigma}^k)^*$ in terms of the natural orbitals $u_{\alpha\sigma}^k$ (eigenvectors of γ) and their occupation numbers $\eta_{k\sigma}$ (eigenvalues of γ). Starting from a physically motivated guess for γ (typically the known $U = 0$ solution), we follow the negative gradient of $E[\gamma]$ with respect to $u_{\alpha\sigma}^k$ and $\eta_{k\sigma}$ until the minimum in the total energy is reached. For this purpose we have used a simple steepest descent procedure, but of course more sophisticated minimization algorithms are also applicable. The gradients $\partial E/\partial u_{\alpha\sigma}^k$ and $\partial E/\partial \eta_{k\sigma}$ are computed straightforwardly from the explicit dependence of $E[\gamma]$ on γ, and the dependence of γ on $u_{\alpha\sigma}^k$ and $\eta_{k\sigma}$. It is important to note that at each step, the occupation numbers $\eta_{k\sigma}$ are normalized in order that they satisfy the ensemble N representability condition [Eq. (11)]. Moreover, the natural orbitals $u_{\alpha\sigma}^k$ are orthonormalized so that $\sum_\alpha (u_{\alpha\sigma}^k)^* u_{\alpha\sigma}^{k'} = \delta_{kk'}$ holds. This ensures that during the entire minimization procedure the eigenvalues $\eta_{k\sigma}$ and the corresponding eigenvectors $u_{\alpha\sigma}^k$ always yield an ensemble N representable density matrix γ.[29]

In the following we consider finite rings with $N_a = 11$ atoms having one conduction-band orbital per atom with energy $\varepsilon_i^s = 0$ and a localized orbital at the impurity site with energy ε_f ($N_o = N_a + 1$ orbitals). The hopping integrals within the conduction states are given by $t_{ij} = -t < 0$ for NN ij and $t_{ij} = 0$ otherwise. Diagonalization of the Hamiltonian $\hat{H}_{\text{cond}} = \sum_{i\sigma} \varepsilon_i^s \hat{a}_{i\sigma}^\dagger \hat{a}_{i\sigma} + \sum_{ij\sigma} t_{ij} \hat{a}_{i\sigma}^\dagger \hat{a}_{j\sigma}$ within the subspace of the conduction states yields the conduction-band spectrum shown in the inset of Fig. 3(b). The corresponding Fermi energy at half-band filling ($N_e = N_a$) is $\varepsilon_F = 0.28t$. Notice that the impurity level couples with all conduction-band Bloch states ($V_{\mathbf{k}f} = V_{sf}/\sqrt{N_a}$ for all $\mathbf{k}$). Since the ground state is a singlet, we focus on states having $\gamma_{ij\uparrow} = \gamma_{ij\downarrow}$. Whenever possible the accuracy of LDFT with the two-level approximation (TLA) W^{2L} is quantified by comparison with exact diagonalizations of the Anderson Hamiltonian (1) using the Lanczos method.[18]

A. From weak to strong correlations

In order to investigate all the interaction regimes from weak to strong correlations, we determine the ground-state density matrix for fixed $t > 0$, $N_a = 11$, $N_e = N_o = 12$, $\varepsilon_f = 0$, and $V_{sf}/t = 0.4$ by varying the Coulomb repulsion parameter U/t. In Fig. 3 results are given for the kinetic, interaction, and total energy, as well as for local properties such as the occupation γ_{ff}, the degree of charge fluctuations $\Gamma_{sf} = (\sum_{\mathbf{k}} |\gamma_{\mathbf{k}f}|^2)^{1/2}$, and the local moment

$$\mu_f = \sqrt{\langle \vec{S}_f \cdot \vec{S}_f \rangle} = \sqrt{3\langle \hat{S}_{fz}^2 \rangle} = \frac{\sqrt{3}}{2} \sqrt{\langle (\hat{n}_{f\uparrow} - \hat{n}_{f\downarrow})^2 \rangle} \tag{43}$$

at the impurity orbital.

Let us first consider the impurity occupation γ_{ff} [Fig. 3(d)]. In the uncorrelated limit ($U = 0$) the impurity orbital is occupied with more than one electron since $\varepsilon_f < \varepsilon_F$. However, notice that $\gamma_{ff} < 2$ due to the hybridization V_{sf} with unoccupied states. As the Coulomb repulsion U increases, a charge transfer from the impurity site to the conduction band occurs for $U \approx \varepsilon_F - \varepsilon_f = 0.28t$, which corresponds to the energy needed to promote an electron from the f orbital to the lowest unoccupied conduction-band state. Further increase of U yields, as expected, a monotonous decrease of the impurity occupation γ_{ff} due to the tendency to minimize $\langle \hat{n}_{f\uparrow} \hat{n}_{f\downarrow} \rangle$ in strongly correlated states. However, the dependence of γ_{ff} on U/t is weak since the double occupations are very efficiently suppressed by correlations when $\varepsilon_f + U \gg \varepsilon_F$. In the present case, where the impurity energy level lies within the conduction band and below ε_F, the f orbital experiences significant charge fluctuations with

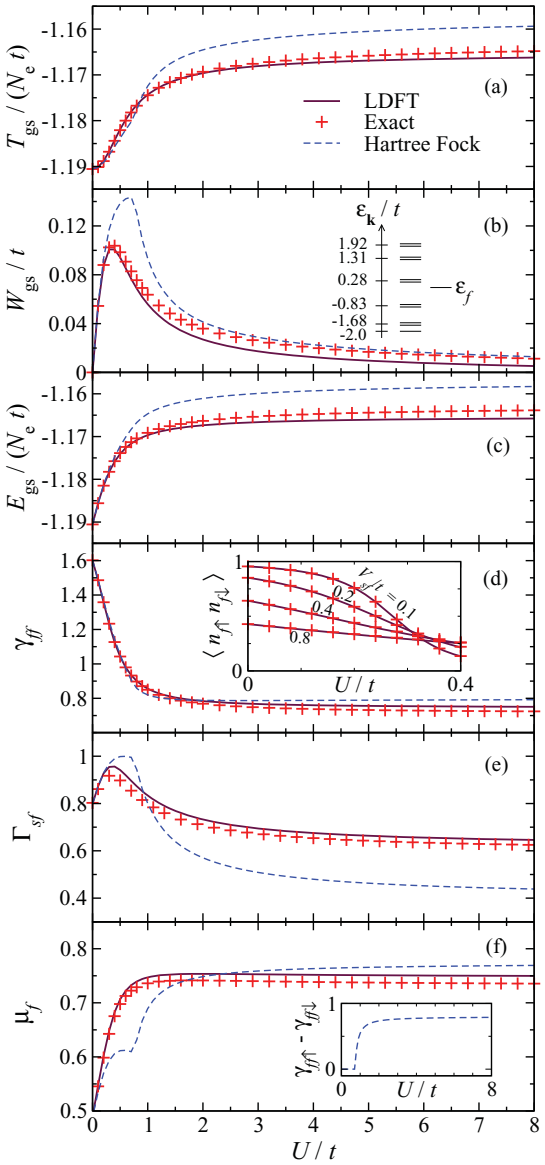

FIG. 3. (Color online) Ground-state properties of a $N_o = 12$ orbital Anderson ring as a function of the Coulomb repulsion U: (a) kinetic energy $T_{\rm gs}$, (b) interaction energy $W_{\rm gs}$, (c) ground-state energy $E_{\rm gs}$, (d) occupation of the impurity orbital γ_{ff}, (e) degree of charge fluctuations $\Gamma_{sf} = (\sum_{\mathbf{k}} |\gamma_{\mathbf{k}f}|^2)^{1/2}$, and (f) impurity magnetic moment μ_f. Lattice density functional theory (LDFT) results obtained within the two-level approximation (full curves) are compared with exact Lanczos diagonalizations (crosses) and unrestricted Hartree-Fock calculations (dashed curves). The inset in (b) illustrates the corresponding single-particle spectrum, where the twofold degeneracy of most conduction-band orbitals is indicated by double lines. The inset of (d) shows $\langle \hat{n}_{f\uparrow}\hat{n}_{f\downarrow}\rangle$ for small U and different V_{sf}, while the inset of (f) shows the broken-symmetry spin-polarization $\gamma_{ff\uparrow} - \gamma_{ff\downarrow}$ of the f orbital in the unrestricted Hartree-Fock approximation.

the conduction-band states [see Fig. 3(e)]. For not too small U/t this corresponds to an $f^1 \leftrightarrow f^0$ intermediate valence state between the singly occupied and empty impurity orbital. Therefore, we have $\gamma_{ff} < 1$ in the strongly correlated limit where double occupations vanish ($U \to +\infty$). Comparison with the exact diagonalizations shows a very good accuracy of LDFT in all interaction regimes. For example, the TLA yields a relative error in γ_{ff} of approximately 0.1% in weakly correlated ground states ($U/t = 0.5$) and of 3.7% in the case of strong electronic correlations ($U/t = 8$).

In Fig. 3(e) results are given for the nondiagonal elements of the density matrix, as measured by the degree of total charge fluctuations between the impurity orbital and the conduction-band states $\Gamma_{sf} = (\sum_{\mathbf{k}} |\gamma_{\mathbf{k}f}|^2)^{1/2}$. For small Coulomb repulsion U/t, where $\gamma_{ff} > 1$, the main impurity charge fluctuations correspond to an $f^2 \leftrightarrow f^1$ intermediate valence state between the singly occupied and doubly occupied impurity orbital. In this range the effective f-level energy $\varepsilon_f + U$ comes closer to ε_F as U increases. This favors charge fluctuations and therefore Γ_{sf} increases with U. The behavior changes, however, as soon as $\gamma_{ff} \leqslant 1$, i.e., for $\varepsilon_f + U > \varepsilon_F$. In this case increasing U tends to suppress double occupations with the corresponding decrease of Γ_{sf}. As already mentioned, in the limit of large U the impurity is in an $f^1 \leftrightarrow f^0$ intermediate valence state ($\gamma_{ff} < 1$). LDFT reproduces these trends quite satisfactorily. Similar to the diagonal matrix element γ_{ff}, the nondiagonal elements Γ_{sf} are well described by the TLA: The relative error in Γ_{sf} is 5% for $U/t = 0.5$ and 3.4% for $U/t = 8$. Comparison with Hartree-Fock results reveals the importance of correlation effects.

The ground-state kinetic energy $T_{\rm gs}$ per electron is displayed in Fig. 3(a). The increase of $T_{\rm gs}$ with increasing U reflects the above-mentioned charge transfer from the impurity to the conduction band for $U \approx \varepsilon_F - \varepsilon_f$. The approximate interaction-energy functional $W^{\rm 2L}$ yields very small relative errors in $T_{\rm gs}$: 0.01% for $U/t = 0.5$ and 0.1% for $U/t = 8$. Since the kinetic-energy functional is taken into account exactly by Eq. (12), the high accuracy of $T_{\rm gs}$ also implies that the TLA gives an overall correct ground-state density matrix $\gamma^{\rm gs}$ as a result of the minimization of the total-energy functional (9).

The local impurity moment $\mu_f = \frac{\sqrt{3}}{2}\sqrt{\langle(\hat{n}_{f\uparrow} - \hat{n}_{f\downarrow})^2\rangle} = \frac{\sqrt{3}}{2}\sqrt{\gamma_{ff} - 2\langle\hat{n}_{f\uparrow}\hat{n}_{f\downarrow}\rangle}$ shown in Fig. 3(f) can be regarded as a measure for the correlation of electrons with opposite spins at the impurity. For a noninteracting system ($U = 0$) μ_f is finite, since there is a finite probability for the f level to be singly occupied. As U increases, the double occupations $\langle\hat{n}_{f\uparrow}\hat{n}_{f\downarrow}\rangle$ become less favorable and μ_f increases due to the increasing correlation ($\mu_f \to \frac{\sqrt{3}}{2}\sqrt{\gamma_{ff}}$ for $U \to +\infty$, since $\langle\hat{n}_{f\uparrow}\hat{n}_{f\downarrow}\rangle$ vanishes). As in previous cases the accuracy of the TLA is quite satisfactory. The relative error in μ_f is about 1.3% for weak correlations ($U/t = 0.5$) and 2% for strongly correlated ground states ($U/t = 8$).

In Fig. 3(b) results are given for the ground-state interaction energy $W_{\rm gs}$. For small U $W_{\rm gs}$ increases with U, since uncorrelated ground states have a maximal average number of double occupations $\langle\hat{n}_{f\uparrow}\hat{n}_{f\downarrow}\rangle_{\rm HF} = \gamma_{ff}^2/4$. In the opposite limit ($U \to +\infty$) $W_{\rm gs}$ tends to zero, which reflects the rapid decrease of $\langle\hat{n}_{f\uparrow}\hat{n}_{f\downarrow}\rangle$. In the crossover region, where the charge transfer from the impurity orbital to the conduction band takes place, one observes a maximum in $W_{\rm gs}$ that is well described by the TLA. For instance, the relative error in $W_{\rm gs}$ is 4.4% for $U/t = 0.5$. However, the relative error in $W_{\rm gs}$ is rather important for large U/t, namely, about 50% for $U/t =$

8. Nevertheless, the absolute error in $W_{\rm gs}$ remains rather small: $(W_{\rm gs}^{\rm TLA} - W_{\rm gs}^{\rm ex})/t \approx 0.007$ for $U/t = 8$. Therefore, the qualitative behavior of $W_{\rm gs}$ is correctly reproduced for all U/t, even in the strongly correlated limit.

The noninteracting limit is investigated in more detail in the inset of Fig. 3(d), which shows the average number of double occupations $\langle \hat{n}_{f\uparrow}\hat{n}_{f\downarrow}\rangle$ at the impurity as a function of U/t for different values of V_{sf}. First of all, the TLA yields very accurate values of $\langle \hat{n}_{f\uparrow}\hat{n}_{f\downarrow}\rangle$ for $U = 0$, where the exact ground state is a single Slater determinant and $\langle \hat{n}_{f\uparrow}\hat{n}_{f\downarrow}\rangle = \gamma_{ff\uparrow}\gamma_{ff\downarrow} = \gamma_{ff}^2/4$. The actual relative error in $\langle \hat{n}_{f\uparrow}\hat{n}_{f\downarrow}\rangle$ is less than 0.001% for $U = 0$. Moreover, the results of the TLA are also very accurate for finite U/t (and all considered V_{sf}/t). This demonstrates that in the noninteracting limit not only the interaction energy $W = U\langle \hat{n}_{f\uparrow}\hat{n}_{f\downarrow}\rangle$, but also the number of f-level double occupations $W/U = \langle \hat{n}_{f\uparrow}\hat{n}_{f\downarrow}\rangle$, is precisely recovered by the TLA.

Fig. 3(c) shows the ground-state energy $E_{\rm gs} = W_{\rm gs} + T_{\rm gs}$ per electron as a function of U/t. Since the TLA reproduces the kinetic energy $T_{\rm gs}$ with high accuracy, and since $T_{\rm gs}$ dominates over $W_{\rm gs}$ in the limit of strong Coulomb repulsion ($W_{\rm gs} \to 0$ for $U \to +\infty$), minor inaccuracies in $W_{\rm gs}$ turn out to be irrelevant for the ground-state energy. In fact the accuracy obtained for $E_{\rm gs}$ is similar to that of the kinetic energy: The relative error in $E_{\rm gs}$ is 0.02% for $U/t = 0.5$, and 0.2% for $U/t = 8$. One concludes that the two-level functional is a good approximation to the interaction energy which provides an accurate description of a variety of ground-state properties in all interaction regimes over the entire range of correlations from weak to strong. Comparison with unrestricted Hartree-Fock results demonstrates the importance of correlation effects and the remarkable improvements achieved by LDFT. It is well known that the limitations of the Hartree-Fock interaction energy $W_{\rm HF} = U\gamma_{ff\uparrow}\gamma_{ff\downarrow}$ render the description of strong correlations impossible. This results in an artificial symmetry breaking with a finite spin polarization $m_f^{\rm HF} = \gamma_{ff\uparrow} - \gamma_{ff\downarrow} \neq 0$ already for $U/t > 0.8$ [see the inset of Fig. 3(f)].[9] This contrasts with the exact ground state and with the results of LDFT, which correspond to a singlet having $m_f = 0$ for all U/t.[28] In opposition to Hartree Fock theory, the TLA does not break the spin symmetry and is thus able to take into account spin and charge fluctuations between the impurity orbital and the conduction-band states for all U/t, even in the strongly correlated limit.

B. Dependence on the impurity valence state

In the previous section the impurity energy ε_f has been kept constant near the Fermi level, which corresponds to an intermediate valence regime. In the following we vary ε_f systematically so as to investigate the ability of LDFT to describe valence changes. The ground-state interaction energy $W_{\rm gs}$, the total energy $E_{\rm gs}$, the occupation of the impurity orbital γ_{ff}, the degree of charge fluctuations $\Gamma_{sf} = (\sum_{\mathbf{k}} |\gamma_{\mathbf{k}f}|^2)^{1/2}$, and the local impurity moment μ_f of an $N_o = 12$ orbital ring with $N_e = 12$ electrons are shown in Fig. 4 for $t > 0$, $U/t = 8$, and $V_{sf}/t = 0.4$.

As long as the single-particle energy $\varepsilon_f + U$ is much smaller than the Fermi level $\varepsilon_F = 0.28t$, the impurity orbital is nearly double occupied ($\gamma_{ff} \approx 2$) since the f-level energy ε_f largely overcomes the repulsion energy U due to the double occupation of the impurity orbital. Consequently, the local impurity moment $\mu_f = \frac{\sqrt{3}}{2}\langle(\hat{n}_{f\uparrow} - \hat{n}_{f\downarrow})^2\rangle^{1/2}$ vanishes and $W_{\rm gs} \approx U$ in this limit. Increasing ε_f, so that the single-particle energy $\varepsilon_f + U$ lies above the conduction-band Fermi energy ε_F, entails a charge transfer from the impurity orbital to the conduction band. For $\varepsilon_f + U \simeq \varepsilon_F$ the impurity occupation fluctuates in an intermediate valence state between f^2 and f^1 which is reflected by the occupation $\gamma_{ff} \approx 1.5$ and by a peak in the degree of charge fluctuations Γ_{sf}. Taking into account the relatively large value of the Coulomb repulsion $U/t = 8$, the double occupations $\langle \hat{n}_{f\uparrow}\hat{n}_{f\downarrow}\rangle$ and the interaction energy $W_{\rm gs}$ tend rapidly to zero if $\varepsilon_f + U > \varepsilon_F$. This implies that $\mu_f \simeq \frac{\sqrt{3}}{2}\sqrt{\gamma_{ff}}$. The impurity orbital is almost exclusively singly occupied as long as ε_f is located well below the Fermi level ($\varepsilon_f < \varepsilon_F$) and above $\varepsilon_F - U$. In this situation, known as the Kondo regime, only virtual charge fluctuations between the impurity and the conduction band are possible.

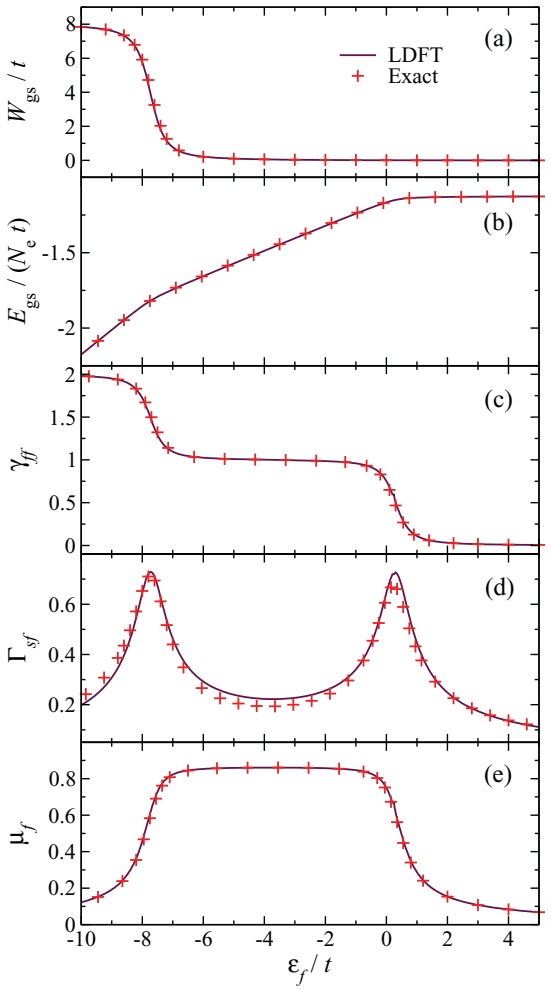

FIG. 4. (Color online) Ground-state properties of a $N_o = 12$ orbital Anderson ring as a function of the impurity energy ε_f: (a) interaction energy $W_{\rm gs}$, (b) ground-state energy $E_{\rm gs}$, (c) occupation of the impurity orbital γ_{ff}, (d) degree of charge fluctuations $\Gamma_{sf} = (\sum_{\mathbf{k}} |\gamma_{\mathbf{k}f}|^2)^{1/2}$, and (e) local impurity moment μ_f. LDFT (full curves) and exact Lanczos diagonalizations (crosses) are compared for $V_{sf}/t = 0.4$ and $U/t = 8$.

When the impurity level ε_f is located near the Fermi level ($\varepsilon_f \approx 0$), the fluctuations of the occupation of the impurity orbital become again favorable. This results in a second peak in the degree of charge fluctuations, which corresponds to the intermediate valence regime where $\gamma_{ff} \approx 0.5$. Finally, increasing ε_f beyond ε_F results in a charge transfer toward the conduction band and thus $\gamma_{ff} \to 0$.

In order to analyze the spin fluctuations at the localized f orbital, which play a central role in the Kondo regime, it is interesting to consider the standard deviation

$$\sigma_{\rm sf} = \sqrt{\langle (\vec{S}_f - \langle \vec{S}_f \rangle)^2 \rangle} \tag{44}$$

of the local spin operator $\vec{S}_f$. In the case of singlet states we have $\langle \vec{S}_f \rangle = 0$ and

$$\sigma_{\rm sf} = \sqrt{\langle \vec{S}_f \cdot \vec{S}_f \rangle} = \mu_f, \tag{45}$$

which coincides with the local moment μ_f [see Eq. (43)]. Consequently, panel (e) of Fig. 4 shows that spin fluctuations dominate especially in the Kondo regime ($\varepsilon_f \ll \varepsilon_F$ and $\varepsilon_f + U \gg \varepsilon_F$) where the f orbital is almost exclusively singly occupied. One concludes that the TLA describes very accurately the degree of spin fluctuations at the impurity.

Comparison with the exact results shows that the TLA describes the Kondo regime, the intermediate valence regime, as well as the crossover region with high accuracy (see Fig. 4). Even in the intermediate valence regime, where the site occupancy γ_{ff}, the degree of charge fluctuations Γ_{sf}, and the local moment μ_f are very sensitive to variations in the impurity level ε_f, the absolute errors remain below 0.04 in γ_{ff}, 0.06 in Γ_{sf}, and 0.03 in μ_f. Moreover, the relative error in the total ground-state energy $E_{\rm gs}$ is less than 0.1% and the absolute error in the Coulomb energy $W_{\rm gs}/U$ less than 0.03.

C. Dependence on the conduction-band width

In Sec. IV A, the TLA has been motivated by showing that this approximation is exact in the limit of a totally degenerate conduction band as well as in the limit of widely separated discrete conduction-band levels. The former corresponds to a vanishing conduction-band width, whereas the latter corresponds to a very large conduction-band hopping integral. It is therefore very interesting to investigate the crossover between the above-mentioned limits by varying the hopping integral t. In Fig. 5, several ground-state properties of an $N_o = 12$ orbital Anderson ring with $N_e = 12$ electrons are given as a function of t for the impurity level $\varepsilon_f/V_{sf} = -1.0$ ($V_{sf} > 0$) and two different values of the Coulomb repulsion $U/V_{sf} = 20$ and $U/V_{sf} = 5$. The calculations with the larger Coulomb repulsion are representative of the most critical intermediate-valence strongly correlated regime, whereas the lower Coulomb repulsion corresponds to a moderately correlated regime.

In the limit of a vanishing hopping integral t the conduction-band states are totally degenerate and $\varepsilon_f - \varepsilon_{\mathbf{k}} = \varepsilon_f = -V_{sf}$ for all $\mathbf{k}$. Since both Coulomb repulsion parameters $U = 5V_{sf}$ and $U = 20V_{sf}$ are much larger than the energy needed to promote an electron from the f orbital to the Fermi level ($\varepsilon_F - \varepsilon_f = V_{sf}$), the average number of f-level double occupations $\langle \hat{n}_{f\uparrow}\hat{n}_{f\downarrow} \rangle$ is quite small for $t = 0$, namely 0.05 for $U = 5V_{sf}$ and 0.003 for $U = 20V_{sf}$. The small value of $\langle \hat{n}_{f\uparrow}\hat{n}_{f\downarrow} \rangle$ together with the charge fluctuations between the impurity orbital and the conduction-band states result in $\gamma_{ff} < 1$, which corresponds to an $f^1 \leftrightarrow f^0$ intermediate valence state. With increasing t the Fermi level increases as $\varepsilon_F = 0.28t$. Therefore, the degree of charge fluctuations Γ_{sf} decreases, while the average number of double occupations remains $\langle \hat{n}_{f\uparrow}\hat{n}_{f\downarrow} \rangle \approx 0$. Consequently, γ_{ff} tends to 1. As we further increase t, the number of double occupations $\langle \hat{n}_{f\uparrow}\hat{n}_{f\downarrow} \rangle$ becomes nonnegligible provided that U is not too large (see the curve for $U/V_{sf} = 5$ in Fig. 5). This results in an increase of the ground-state interaction energy $W_{\rm gs}$, the f-level occupation γ_{ff}, and the degree of charge fluctuations Γ_{sf}, as well as in a reduction of the local magnetic moment μ_f at the impurity site.

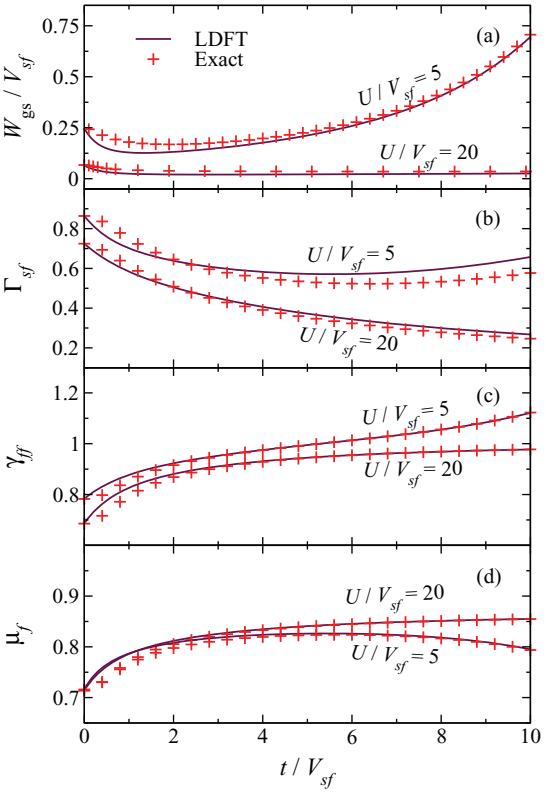

FIG. 5. (Color online) Ground-state properties of a $N_o = 12$ orbital Anderson ring as a function of the conduction-band hopping integral t: (a) interaction energy $W_{\rm gs}$, (b) degree of charge fluctuations $\Gamma_{sf} = (\sum_{\mathbf{k}} |\gamma_{\mathbf{k}f}|^2)^{1/2}$, (c) impurity-orbital occupation γ_{ff}, and (d) local impurity moment μ_f. LDFT (full curves) and exact Lanczos diagonalizations (crosses) are compared for $\varepsilon_f/V_{sf} = -1.0$ ($V_{sf} > 0$) and two different Coulomb repulsion parameters, $U/V_{sf} = 20$ and $U/V_{sf} = 5$.

Comparison between LDFT and exact results shows a very good agreement. Besides reproducing the $t = 0$ and $t \to \infty$ limits the TLA remains accurate for all finite values of the conduction-band width (see Fig. 5). The absolute errors introduced by the TLA are less than $0.056V_{sf}$ for the interaction energy $W_{\rm gs}$, 0.078 for the degree of charge fluctuations Γ_{sf}, 0.046 for the site occupancy γ_{ff}, and 0.025 for the local moment μ_f. Appreciable discrepancies are only

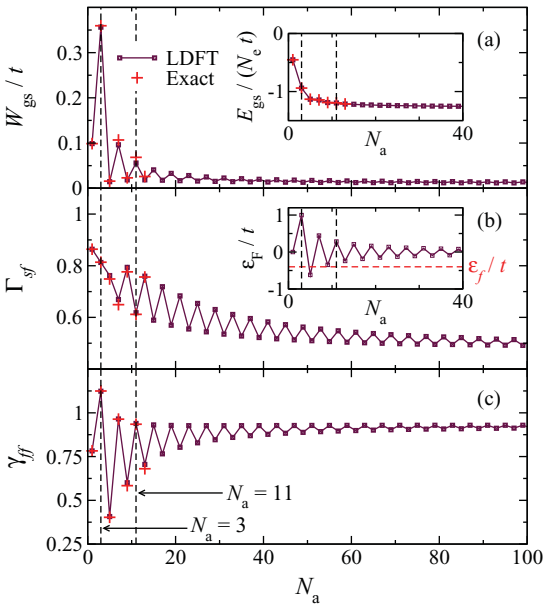

FIG. 6. (Color online) Ground-state properties of Anderson rings as a function of the number of sites N_a (even $N_o = N_a + 1$ orbitals). The model parameters are $t > 0$, $\varepsilon_f/t = -0.4$, $V_{sf}/t = 0.4$, $U/t = 2$, and $N_e = N_o = N_a + 1$. Results are given for (a) the interaction energy W_{gs}, (b) the degree of charge fluctuations $\Gamma_{sf} = (\sum_{\mathbf{k}} |\gamma_{\mathbf{k}f}|^2)^{1/2}$, and (c) the occupation of the impurity orbital γ_{ff}. The inset in (a) shows the ground-state energy E_{gs}, while the inset in (b) shows the size dependence of the conduction-band Fermi level ε_F. For $N_a \leqslant 13$ the LDFT results (dots) are compared with exact Lanczos diagonalizations (crosses). The lines between the dots are a guide to the eye. The dashed vertical lines highlight the results for $N_a = 3$ and $N_a = 11$.

found for $t \simeq V_{sf}$ and in the case of Γ_{sf} for moderate values of the Coulomb repulsion (see Fig. 5).

D. Dependence on system size

Since the TLA is based on the exact solution of a two-level problem, it is important to investigate its behavior as a function of system size. To this aim we consider rings having $N_a - 1$ simple metal atoms and one impurity atom ($N_o = N_a + 1$ orbitals). In Fig. 6 results are given for $N_a \leqslant 100$ and $N_e = N_o = N_a + 1$ electrons taking the energy of all atomic s levels $\varepsilon_i^s = 0$, NN hopping integral $t_{ij} = -t < 0$, impurity level $\varepsilon_f/t = -0.4$, sf hybridization $V_{sf}/t = 0.4$, and Coulomb repulsion $U/t = 2$. This corresponds to an intermediate correlated regime. Notice that only odd values for N_a are considered, since for an even number of atoms N_a the Hamiltonian (1) becomes reducible. In this case some conduction-band orbitals are decoupled from the impurity orbital. Moreover, the number of electrons $\tilde{N}_e$ in the irreducible block that couples with the impurity orbital depends on U/t, V_{sf}/t and ε_f/t. In particular, $\tilde{N}_e$ can be odd, which is beyond the domain of application of the present functional derived for singlet states with an even number of electrons.

The results for the ground-state properties (Fig. 6) show an interesting dependence on the chain length N_a or the number of orbitals $N_o = N_a + 1$. In the case of E_{gs}/N_e and W_{gs} the convergence to the infinite-length limit is reached rather rapidly for $N_a \simeq 20$. In contrast, finite-size effects appear to be stronger in the case of γ_{ff} and Γ_{sf}, which converge only for $N_a \simeq 80$–100. On top of this overall length dependence, one observes important *super-even* oscillations: W_{gs}, Γ_{sf}, and γ_{ff} oscillate as a function of the even number of orbitals N_o or electrons N_e depending on whether $N_o = N_e$ is $4m$ or $4m + 2$ with m integer. The average f-level occupation and Coulomb repulsion are systematically larger (smaller) for $N_e/2$ even (odd), while the degree of sf charge fluctuations follow the opposite trend (see Fig. 6). These oscillations can be correlated to the oscillations of the Fermi energy of the conduction band ε_F as a function of N_a [see the inset of Fig. 6(b)]. Indeed, the larger the energy difference $\varepsilon_F - \varepsilon_f > 0$ is, the lower is the energy $2\varepsilon_f + U$ of two electrons occupying the localized f level. Therefore, a maximum in ε_F corresponds to maxima in both γ_{ff} and W_{gs} (e.g., $N_a = 11$ indicated by a vertical dashed line). On the other hand, small values of $\varepsilon_F - \varepsilon_f$ enhance the charge fluctuations between the impurity orbital and the conduction band. Thus, minima in ε_F imply maxima in Γ_{sf} corresponding to an $f^1 \leftrightarrow f^0$ intermediate valence state. The triangle ($N_a = 3$, vertical dashed line) appears an exception which can be understood by noticing that in this case the energy difference $\varepsilon_F - \varepsilon_f$ is comparable with the Coulomb repulsion U, which implies significant double occupation of the impurity level. This opens the possibility of additional $f^2 \leftrightarrow f^1$ charge fluctuations and thus explains the relatively large Γ_{sf} despite the fact that ε_F shows a local maximum.

In the limit of a large number of atoms N_a the difference $\varepsilon_F - \varepsilon_f$ tends to the constant $0.4t$; i.e., the impurity orbital is located well below the Fermi level. Since the Coulomb repulsion is much larger ($U/t = 2$), the number of double occupations $\langle \hat{n}_{f\uparrow} \hat{n}_{f\downarrow} \rangle$ and thus the interaction energy W_{gs} become negligible. Moreover, the f-level occupation converges to a value $\gamma_{ff} < 1$, which reflects a significant degree of charge fluctuations $\Gamma_{sf} \approx 0.5$. Consequently, this limit corresponds to an $f^1 \leftrightarrow f^0$ intermediate valence state between the singly occupied and empty impurity orbital.

Comparison with the exact results for $N_a \leqslant 13$ shows that the TLA gives the correct trends as a function of N_a for all considered ground-state properties. The absolute error in the ground-state density-matrix elements is found to be less than 0.025 for γ_{ff} and less than 0.02 for Γ_{sf}. Moreover, the interaction energy W_{gs} is reproduced with an accuracy of $0.012t$ or better. Consequently, the relative error in the ground-state energy E_{gs} is always less than 0.3% [see the inset of Fig. 6(a)]. This suggests that the minimization of the total-energy functional E using the TLA yields a good approximation to the ground-state density matrix and the properties derived from it for systems with an arbitrary number of atoms.

So far only one-dimensional systems in a ring geometry have been studied. Nevertheless, the present TLA is directly applicable to higher dimensions, since no 1D specific assumption has been made throughout its derivation. In order to demonstrate it, we consider in Fig. 7 the two-dimensional square lattice. LDFT results for the ground-state interaction energy W_{gs} and the local impurity moment μ_f are compared with Lanczos exact diagonalizations in the case of an $N_a = 3 \times 3$ periodic cluster with the impurity at the center. To this aim representative model parameters $t > 0$, $\varepsilon_f/t = -0.4$,

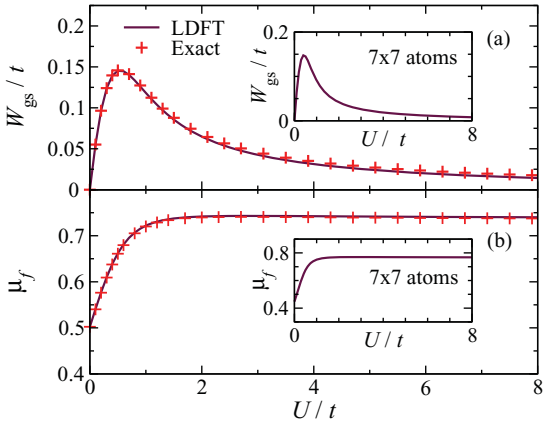

FIG. 7. (Color online) (a) Ground-state interaction energy W_{gs} and (b) local moment μ_f of the $N_a = 3 \times 3$ atoms Anderson square lattice as a function of the Coulomb repulsion U. In the lattice the additional impurity orbital is located at the center while the system parameters are $t > 0$, $\varepsilon_f/t = -0.4$, $V_{sf}/t = 0.4$, and $N_e = N_a + 1 = 10$. The LDFT results (dots) are compared with exact Lanczos diagonalizations (crosses). In the insets the corresponding electronic properties for the $N_a = 7 \times 7$ atom lattice having an additional impurity orbital at the center and $N_e = 50$ electrons are presented.

$V_{sf}/t = 0.4$, and $N_e = N_o = N_a + 1 = 12$ are considered and the Coulomb repulsion U/t is varied. The results show that the TLA reproduces with a high accuracy the ground-state properties of the Anderson model also in 2D, over the entire range from weak to strong correlations. For a weak Coulomb repulsion $U/t = 0.5$ the absolute error in W_{gs} is less than $0.0005t$, while the relative error in the local moment μ_f is less than 0.2%. In the case of strong correlations ($U/t = 8$) the TLA yields an absolute error of $0.003t$ for W_{gs} and a relative error of 0.4% for μ_f. This demonstrates that the TLA constitutes a powerful tool for higher dimensional versions of the Anderson single-impurity model as well. In the insets of Fig. 7 the LDFT results for the $N_a = 7 \times 7$ atom lattice are presented, in order to illustrate the applicability of the TLA for larger two-dimensional systems.

VI. SUMMARY AND OUTLOOK

A lattice density functional theory (LDFT) of the single-impurity Anderson model has been developed. To this aim a simple explicit approximation to the central interaction-energy functional $W[\gamma]$ has been proposed, which is based on exact two-level results and general symmetry properties. The invariance of the functional $W[\gamma]$ under unitary transformations among the conduction states has been exploited to identify the *single* symmetry-adapted conduction state with which the localized impurity orbital experiences direct charge fluctuations. This transformation is central to our ansatz, since only two single-particle states, namely, the above-mentioned symmetry-adapted conduction-band state and the impurity orbital, are taken explicitly into account in the derivation of the functional dependence of $W[\gamma]$. A simple spin-restricted analytical approximation to $W[\gamma]$ for singlet systems has been derived on the basis of the solution of the two-level Anderson model. This so-called two-level approximation (TLA) has been shown to be exact in two opposite limits: a totally degenerate conduction band and a conduction band with widely separated discrete levels. Applications to finite rings having $N_a \leqslant 100$ sites have demonstrated that the TLA gives accurate results for the electronic ground-state properties of the Anderson model (kinetic, interaction, and total energy, degree of charge fluctuations, impurity-level occupancy, and local impurity magnetic moment) in all parameter ranges. The regimes of strong and weak correlations, as well as the Kondo and the intermediate valence regimes, have been successfully described. In addition, applications to two-dimensional periodic clusters have shown that the TLA is also accurate for higher dimensional systems. One concludes that LDFT with the TLA not only provides an alternative perspective to the subtle problem of strong electron correlations and a remarkable qualitative improvement over mean-field approximations, but also that it should open the way to novel applications and extensions.[30]

The functional dependence of $W[\gamma]$ on the density-matrix elements provides new insights into the form of the interaction-energy functional for more realistic lattice models. At first sight, it might be quite astonishing that a simple approximation derived from a two-level system is capable of describing the interaction energy in large systems with complex conduction-band electronic structure. This is probably a consequence of the form of the two-particle interactions in the Anderson Hamiltonian, where, as in the Hubbard model, only the local interaction of two electrons at the impurity orbital is taken into account. In fact, neglecting the two-particle interactions between electrons in different orbitals has been proven to be a most successful approach in order to focus on the physics of the magnetic degree of freedom of the impurity and its coupling to the relevant conduction states close to the Fermi energy. From this perspective it is physically reasonable to expect that the functional dependence of the interaction energy $W[\gamma]$ can be grasped in terms of the density-matrix elements that describe the local geometry of the impurity and its coupling to the metallic environment. The TLA constitutes a first encouraging ansatz for choosing the appropriate conduction-band states which are coupled to the impurity. An interesting route for future improvements would be to develop a systematic method of extending the set of relevant conduction-band states involved in the derivation of $W[\gamma]$. In this way more realistic multiband impurity models could be addressed.

In this work, the derivation of the TLA has been restricted to spin-unpolarized systems with $N_{e\uparrow} = N_{e\downarrow}$. Consequently, the ground-state density matrix has been obtained by minimizing the total-energy functional $E[\gamma]$ with respect to density matrices satisfying $\gamma_{ij\uparrow} = \gamma_{ij\downarrow}$ for all sites ij. This is justified by the fact that the ground state is known to be a singlet.[28] However, it is also true that the spin restriction precludes the present approximation from being applied to systems with spin-dependent charge distributions. An extension to spin-polarized density matrices is most desirable, since it would allow us to investigate systems with an odd number of electrons, to quantify the effect of an external magnetic field, and to determine the electronic properties in excited states with $S \geqslant 1$. Research in this direction is currently in progress.

APPENDIX: INTERACTION-ENERGY FUNCTIONAL OF THE TWO-LEVEL PROBLEM

This Appendix is devoted to the derivation of the interaction-energy functional $W^{2L}[\gamma]$ of a two-level system (singlet state). The derivation involves three main steps. First, we consider pure-state N representable density matrices γ with the most important particle number $N_e = 2$ (half-band filling). Second, we extend the functional to ensemble N representable γ. Finally, the more general case of fractional particle numbers is considered.

A. Pure-state N representable γ with particle number $N_e = 2$

For pure-state N representable density matrices γ the minimization involved in the definition of $W^{2L}[\gamma]$ yields $w_m = 1$ for one m and $w_{m'} = 0$ for $m' \neq m$ (pure state) [see Eq. (31)]. Consequently, for any given density matrix elements γ_{ff}, γ_{ss}, and γ_{sf} with $\gamma_{ff} + \gamma_{ss} = 2$, the minimum number of f-level double occupations $\langle \hat{n}_{f\uparrow}\hat{n}_{f\downarrow}\rangle$ can be obtained by minimizing the functional

$$\begin{aligned} A[|\Psi\rangle] = {} & \langle\Psi|\hat{n}_{f\uparrow}\hat{n}_{f\downarrow}|\Psi\rangle - \varepsilon\left(\langle\Psi|\Psi\rangle - 1\right) \\ & + \lambda_{ff}\left(\langle\Psi|\sum_\sigma \hat{f}^\dagger_\sigma \hat{f}_\sigma|\Psi\rangle - \gamma_{ff}\right) \\ & + \lambda_{sf}\left(\langle\Psi|\sum_\sigma \hat{c}^\dagger_{s\sigma} \hat{f}_\sigma|\Psi\rangle - \gamma_{sf}\right) \\ & + \lambda^*_{sf}\left(\langle\Psi|\sum_\sigma \hat{f}^\dagger_\sigma \hat{c}_{s\sigma}|\Psi\rangle - \gamma_{fs}\right) \end{aligned} \tag{A1}$$

with respect to states $|\Psi\rangle$ in the $N_e = 2$ singlet subspace. The Lagrange multiplier ε, $\lambda_{ff} \in \mathbb{R}$, and $\lambda_{sf} \in \mathbb{C}$ in Eq. (A1) assure that $|\Psi\rangle$ is normalized and yields the given γ. Without loss of generality one may assume $\gamma_{sf} \in \mathbb{R}$. Should the nondiagonal element γ_{sf} be complex, then the phase of the delocalized orbital $\hat{c}^\dagger_{s\sigma}$ can be changed to render γ_{sf} real without changing the number of f-level double occupations. Consequently, $\lambda_{sf} \in \mathbb{R}$ and the variational equation for a stationary $|\Psi\rangle$ that minimizes $A[|\Psi\rangle]$ reads

$$\left(\lambda_{ff}\sum_\sigma \hat{n}_{f\sigma} + \lambda_{sf}\sum_\sigma[\hat{c}^\dagger_{s\sigma}\hat{f}_\sigma + \hat{f}^\dagger_\sigma\hat{c}_{s\sigma}] + \hat{n}_{f\uparrow}\hat{n}_{f\downarrow} - \varepsilon\right)|\Psi\rangle = 0. \tag{A2}$$

In other words, the particular state $|\Psi\rangle$ having the minimum double occupations for a fixed density matrix γ (i.e., $W^{2L}[\gamma] = \langle\Psi|\hat{n}_{f\uparrow}\hat{n}_{f\downarrow}|\Psi\rangle$) is an eigenstate of a two-level Anderson model (A2) with real parameters λ_{ff} and λ_{sf}. This implies that the most general singlet

$$\begin{aligned} |\Psi\rangle = {} & \alpha_1 \hat{c}^\dagger_{s\uparrow}\hat{c}^\dagger_{s\downarrow}|\mathrm{vac}\rangle + \alpha_2 \hat{f}^\dagger_\uparrow \hat{f}^\dagger_\downarrow|\mathrm{vac}\rangle \\ & + \frac{\alpha_3}{\sqrt{2}}(\hat{f}^\dagger_\uparrow\hat{c}^\dagger_{s\downarrow} - \hat{f}^\dagger_\downarrow\hat{c}^\dagger_{s\uparrow})|\mathrm{vac}\rangle \end{aligned} \tag{A3}$$

has real expansion coefficients α_i. The constraints $\gamma_{\alpha\beta} = \langle\Psi|\sum_\sigma \hat{c}^\dagger_{\alpha\sigma}\hat{c}_{\beta\sigma}|\Psi\rangle$ in terms of α_i read

$$\begin{aligned} 2\alpha_2^2 + \alpha_3^2 = \gamma_{ff}, \quad 2\alpha_1^2 + \alpha_3^2 = \gamma_{ss} = 2 - \gamma_{ff}, \\ \sqrt{2}(\alpha_1 + \alpha_2)\alpha_3 = \gamma_{sf}. \end{aligned} \tag{A4}$$

From Eq. (A3) it follows that $\alpha_2^2 = \langle\hat{n}_{f\uparrow}\hat{n}_{f\downarrow}\rangle$. Solving the set of Eqs. (A4) for α_2^2 and minimizing it one obtains

$$\begin{aligned} \min_{\substack{\Psi\to\gamma \\ \text{singlet}}} \langle\Psi|\hat{n}_{f\uparrow}\hat{n}_{f\downarrow}|\Psi\rangle &= D^{(2)}(\gamma_{ff},\gamma_{sf}) \\ &= \frac{\gamma_{ff}}{2} - \frac{|\gamma_{sf}|^2/4}{1 - \sqrt{|\gamma^0_{sf}|^2 - |\gamma_{sf}|^2}}, \end{aligned} \tag{A5}$$

where we have used that

$$\gamma^0_{sf} = \gamma^0_{sf\uparrow} + \gamma^0_{sf\downarrow} = \sqrt{\gamma_{ff}(2 - \gamma_{ff})} \tag{A6}$$

[see Eq. (16)]. This completes the derivation of the interaction-energy functional W^{2L} for pure singlet states having $N_e = 2$. Notice that the domain of definition of $D^{(2)}$ in Eq. (A5) coincides with the domain of definition of the more general ensemble N representable γ [see Eqs. (14)–(16)]. In other words the domains of definition of pure and ensemble N representable γ are identical in the two-level subspace.

B. Ensemble N representable γ with $N_e = \gamma_{ss} + \gamma_{ff} = 2$

While $D^{(2)}(\gamma_{ff},\gamma_{sf})$ in Eq. (A5) yields the minimum of $\langle\hat{n}_{f\uparrow}\hat{n}_{f\downarrow}\rangle$ for pure states it need not yield the minimum Coulomb interaction in the larger domain of ensemble N representable γ. This problem is solved in the following. First of all, one observes that the minima of Eq. (A5) as a function of γ_{sf} for fixed γ_{ff} are located at

$$\gamma^\infty_{sf} = \begin{cases} \sqrt{2\gamma_{ff}(1-\gamma_{ff})} & \text{if} \quad \gamma_{ff} \leqslant 1, \\ \sqrt{2(2-\gamma_{ff})(\gamma_{ff}-1)} & \text{if} \quad \gamma_{ff} > 1, \end{cases} \tag{A7}$$

and are given by

$$D^{(2)}_\infty(\gamma_{ff}) = D^{(2)}\left(\gamma_{ff},\gamma^\infty_{sf}\right) = \begin{cases} 0 & \text{if} \quad \gamma_{ff} \leqslant 1, \\ \gamma_{ff} - 1 & \text{if} \quad \gamma_{ff} > 1. \end{cases} \tag{A8}$$

For $|\gamma_{sf}| \geqslant \gamma^\infty_{sf}$ the minimization of double occupations $\langle\hat{n}_{f\uparrow}\hat{n}_{f\downarrow}\rangle = \sum_m w_m\langle\Psi_m|\hat{n}_{f\uparrow}\hat{n}_{f\downarrow}|\Psi_m\rangle$ over the states $|\Psi_m\rangle$ and weights w_m satisfying $\gamma_{\alpha\beta} = \sum_m w_m\langle\Psi_m|\sum_\sigma \hat{c}^\dagger_{\alpha\sigma}\hat{c}_{\beta\sigma}|\Psi_m\rangle$ yields a pure state (i.e., $w_{m'} = 1$ for m' equal to some m and 0 otherwise). Therefore, $D^{(2)}(\gamma_{ff},\gamma_{sf})$ is given by Eq. (A5) for $\gamma^0_{sf} \geqslant |\gamma_{sf}| \geqslant \gamma^\infty_{sf}$. For $|\gamma_{sf}| < \gamma^\infty_{sf}$ we consider the mixed state

$$\hat{\Gamma} = t|\Psi_1\rangle\langle\Psi_1| + (1-t)|\Psi_2\rangle\langle\Psi_2| \tag{A9}$$

with $t \in [0,1]$. The two states $|\Psi_1\rangle$ and $|\Psi_2\rangle$ satisfy $\langle\Psi_i|\sum_\sigma \hat{f}^\dagger_\sigma\hat{f}_\sigma|\Psi_i\rangle = \gamma_{ff}$ and $\langle\Psi_i|\sum_\sigma \hat{c}^\dagger_{s\sigma}\hat{f}_\sigma|\Psi_i\rangle = \pm\gamma^\infty_{sf}$, where the + (−) sign corresponds to $i = 1$ ($i = 2$). It is easy to see that for $t = \frac{1}{2}(1 + \gamma_{sf}/\gamma^\infty_{sf})$ the mixed state $\hat{\Gamma}$ satisfies both conditions

$$\mathrm{Tr}\left\{\hat{\Gamma}\sum_\sigma \hat{f}^\dagger_\sigma\hat{f}_\sigma\right\} = t\gamma_{ff} + (1-t)\gamma_{ff} = \gamma_{ff} \tag{A10}$$

and

$$\mathrm{Tr}\left\{\hat{\Gamma}\sum_\sigma \hat{c}^\dagger_{s\sigma}\hat{f}_\sigma\right\} = t\gamma^\infty_{sf} - (1-t)\gamma^\infty_{ff} = \gamma_{sf}. \tag{A11}$$

The average f-level double occupation then reads

$$\langle \hat{n}_{f\uparrow}\hat{n}_{f\downarrow}\rangle = tD^{(2)}\left(\gamma_{ff},\gamma_{sf}^{\infty}\right) + (1-t)D^{(2)}(\gamma_{ff},-\gamma_{sf}^{\infty}) = D^{(2)}\left(\gamma_{ff},\gamma_{sf}^{\infty}\right) = D_{\infty}^{(2)}(\gamma_{ff}). \quad \text{(A12)}$$

Since this value of $D_{\infty}^{(2)}(\gamma_{ff})$ coincides with the absolute minimum of $\langle \hat{n}_{f\uparrow}\hat{n}_{f\downarrow}\rangle$ for a fixed impurity occupation γ_{ff} [see Eq. (18)], one concludes that

$$D^{(2)}(\gamma_{ff},\gamma_{sf}) = D_{\infty}^{(2)}(\gamma_{ff}) \quad \text{for} \quad |\gamma_{sf}| < \gamma_{sf}^{\infty}. \quad \text{(A13)}$$

By extending the domain of definition to ensemble N representable γ, the minimum number of f-level double occupations $D^{(2)}(\gamma_{ff},\gamma_{sf})$ has been reduced with respect to the result for pure states given by Eq. (A5). Putting Eqs. (A5) for $|\gamma_{sf}| \geqslant \gamma_{sf}^{\infty}$ and (A13) together yields the Eq. (32) for W^{2L} given in the main text (Sec. IV C).

C. Fractional particle numbers $N_e = \gamma_{ss} + \gamma_{ff}$

For most systems the two-level block is not isolated and therefore the number of electrons $N_e = \gamma_{ss} + \gamma_{ff}$ need not be an integer. We consider explicitly the case $0 \leqslant \gamma_{ss} + \gamma_{ff} \leqslant 2$. The expressions for $2 < N_e \leqslant 4$ can be obtained by exploiting the electron-hole symmetry (19). In the case of singlet states we consider

$$\hat{\Gamma} = \frac{N_e}{2}\hat{\Gamma}^{(2)} + \left(1 - \frac{N_e}{2}\right)|\text{vac}\rangle\langle\text{vac}|, \quad \text{(A14)}$$

where $\hat{\Gamma}^{(2)} = \sum_m w_m |\Psi_m^{(2)}\rangle\langle\Psi_m^{(2)}|$ is the superposition of two-particle singlet states $|\Psi_m^{(2)}\rangle$, and $|\text{vac}\rangle$ is the empty two-level state. The coefficients $N_e/2$ and $1 - N_e/2$ ensure the correct particle number $\text{Tr}\{\hat{\Gamma}\hat{N}_e\} = N_e$. It is important to recall that the constraint

$$\text{Tr}\left\{\hat{\Gamma}\sum_{\sigma}\hat{c}_{\alpha\sigma}^{\dagger}\hat{c}_{\beta\sigma}\right\} = \gamma_{\alpha\beta} \quad \text{(A15)}$$

on $\hat{\Gamma}$ implies the corresponding constraint

$$\frac{2}{N_e}\gamma_{\alpha\beta} = \text{Tr}\left\{\hat{\Gamma}^{(2)}\sum_{\sigma}\hat{c}_{\alpha\sigma}^{\dagger}\hat{c}_{\beta\sigma}\right\} = \sum_m w_m \langle\Psi_m^{(2)}|\sum_{\sigma}\hat{c}_{\alpha\sigma}^{\dagger}\hat{c}_{\beta\sigma}|\Psi_m^{(2)}\rangle \quad \text{(A16)}$$

on $\hat{\Gamma}^{(2)}$. The average of f-level double occupations depends only on $\hat{\Gamma}^{(2)}$; i.e.,

$$\langle \hat{n}_{f\uparrow}\hat{n}_{f\downarrow}\rangle = \text{Tr}\{\hat{\Gamma}\hat{n}_{f\uparrow}\hat{n}_{f\downarrow}\} = \frac{N_e}{2}\text{Tr}\{\hat{\Gamma}^{(2)}\hat{n}_{f\uparrow}\hat{n}_{f\downarrow}\}. \quad \text{(A17)}$$

Consequently, minimizing $\langle \hat{n}_{f\uparrow}\hat{n}_{f\downarrow}\rangle$ over all mixed states $\hat{\Gamma}$ satisfying (A15) is equivalent to minimizing $\langle \hat{n}_{f\uparrow}\hat{n}_{f\downarrow}\rangle$ over all mixed states of the form $\hat{\Gamma}^{(2)} = \sum_m w_m |\Psi_m^{(2)}\rangle\langle\Psi_m^{(2)}|$ satisfying (A16). Since the singlet states $|\Psi_m^{(2)}\rangle$ have definite particle number $N_e = 2$, one obtains that the minimum number of f-level double occupations $D(\gamma_{ff},\gamma_{ss},\gamma_{sf})$ for a particle number $0 \leqslant N_e \leqslant 2$ is given by

$$D(\gamma_{ff},\gamma_{ss},\gamma_{sf}) = \frac{N_e}{2}D^{(2)}\left(\frac{2\gamma_{ff}}{N_e},\frac{2\gamma_{sf}}{N_e}\right), \quad \text{(A18)}$$

where $D^{(2)}$ denotes the minimum f-level double occupations for $N_e = 2$ (see previous subsection). Using Eqs. (A6), (A7), (A8), and (A13) and the electron-hole symmetry (19) for the case $2 < N_e \leqslant 4$, one obtains that the two-level interaction-energy functional W^{2L} for fractional particle numbers reads

$$W^{2L}(\gamma_{ff},\gamma_{ss},\gamma_{sf}) = \begin{cases} U\left(\frac{\gamma_{ff}}{2} - \frac{|\gamma_{sf}|^2/4}{\min\{\frac{N_e}{2},2-\frac{N_e}{2}\}-\sqrt{|\gamma_{sf}^0|^2-|\gamma_{sf}|^2}}\right) & \text{if} \quad |\gamma_{sf}| > \gamma_{sf}^{\infty}, \\ W_{\infty}(\gamma_{ff},\gamma_{ss}) & \text{if} \quad |\gamma_{sf}| \leqslant \gamma_{sf}^{\infty}. \end{cases} \quad \text{(A19)}$$

According to the constraint (16), the maximum degree of sf charge fluctuations γ_{sf}^0 is given by Eq. (39) in the main text. One also finds that the degree of charge fluctuations γ_{sf}^{∞} in the strongly correlated limit is given by Eq. (40) and the corresponding interaction energy W_{∞} by Eq. (41). This completes the derivation for the singlet two-level interaction-energy functional $W^{2L}[\gamma]$ used throughout this work as given by Eq. (38).

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[22]The convexity of the ground-state energy $E_{\rm gs}(N_e)$ can be expressed in terms of the chemical potential as $\mu(N_e+1) > \mu(N_e)$. This behavior is reasonable for many-body systems with a repulsive Coulomb interaction because the energy $\Delta E = E_{\rm gs}(N_e+1) - E_{\rm gs}(N_e)$ associated with adding a particle increases with increasing the number of particles N_e.

[23]A necessary and sufficient condition for a Hermitic matrix to be positive definite is that all principal determinants on the diagonal be positive. Applying this to γ and $1-\gamma$ implies $\gamma_{ff\sigma}\gamma_{\mathbf{k}\mathbf{k}\sigma} - \gamma^2_{\mathbf{k}f\sigma} \geqslant 0$ and $(1-\gamma_{ff\sigma})(1-\gamma_{\mathbf{k}\mathbf{k}\sigma}) - \gamma^2_{\mathbf{k}f\sigma} \geqslant 0$, from which the inequalities (14) and (15) follow.

[24]For $\gamma_{ff} \leqslant 1$ the minimum number of double occupations $\langle \hat{n}_{f\uparrow}\hat{n}_{f\downarrow}\rangle$ is zero, since one may choose $\gamma_{ff\uparrow} = \gamma_{ff}$ and $\gamma_{ff\downarrow} = 0$. For $\gamma_{ff} > 1$ we have $\min\{\langle \hat{n}_{f\uparrow}\hat{n}_{f\downarrow}\rangle\} = \gamma_{ff} - 1$, which corresponds to $\gamma_{ff\uparrow} = 1$ and $\gamma_{ff\downarrow} = \gamma_{ff} - 1$. This leads to Eq. (18).

[25]It is worth noting that the two considered unitary transformations within the conduction band, namely $S'_{\mathbf{k}s\sigma} \sim V_{\mathbf{k}f}$ in Sec. IV B(1) and $S_{\mathbf{k}s\sigma} \sim \gamma_{\mathbf{k}f\sigma}$ in Sec. IV A, are equivalent for the ground-state density matrix $\gamma^{\rm gs}$ of an Anderson model with a totally degenerate conduction band. However, they are conceptually different and they are not equivalent in general for an arbitrary γ. In Sec. IV A the transformation $\hat{S}_\sigma$ has been applied for a given γ in order that the impurity experience direct charge fluctuations only with one conduction-band state. In this context there is no reference to an explicit Hamiltonian and any reference to matrix elements such as $V_{\mathbf{k}f}$ would be inappropriate. In contrast, in Sec. IV B(1) the starting point is the Hamiltonian $\hat{H}$ and the unitary transformation $\hat{S}'_\sigma$ is applied in order to decouple the Hamiltonian in two parts. The first block is the two-level subspace containing the impurity level $|\, f_\sigma \,\rangle$ and the orbital $|\, b_{s\sigma} \,\rangle$, and the second one refers to the rest of the conduction band.

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[27]Notice that the phase of the delocalized orbital $\hat{c}^\dagger_{s\sigma}$ can always be changed to render V_{sf} real and positive.

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[29]It has been shown in Ref. 14 that the natural orbitals $u^k_{\alpha\sigma}$ of the ground-state density matrix γ^{gs} satisfy the eigenvalue equation $\sum_\beta (H^{\rm eff}_{\alpha\beta\sigma} - \lambda_{k\sigma}\delta_{\alpha\beta})u^k_{\beta\sigma} = 0$, where the effective single-particle Hamiltonian is given by $H^{\rm eff}_{\alpha\beta\sigma} = \delta E/\delta\gamma_{\beta\alpha\sigma}$. Instead of solving this single-particle equation we use a direct energy minimization method exploiting the explicit dependence of the two-level functional $W^{2L}[\gamma]$ on γ. In this sense our minimization approach is orbital free.

[30]Notice that the present approximation gives in general results with a similar qualitative behavior as the second-moment approximation proposed in Ref. 13, which can also be shown to be exact for a two-level system.