

Local density approximation combined with Gutzwiller method for correlated electron systems: Formalism and applications

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We report in detail our *ab initio* local density approximation (LDA)+Gutzwiller method, in which the Gutzwiller variational approach is naturally incorporated with the density-functional theory through the “Gutzwiller density-functional theory” (which is a generalization of original Kohn-Sham formalism). This method can be used for ground-state determination of electron systems ranging from weakly correlated metal to strongly correlated insulators with long-range ordering. We will show that its quality for ground state is as high as that by dynamic mean-field theory, and yet it is computationally much cheaper. In addition, the method is fully variational, the charge-density self-consistency can be naturally achieved, and the quantities, such as total energy and linear response, can be accurately obtained similarly as with LDA-type calculations. Applications on several typical systems are presented, and the characteristic aspects of this method are clarified. The obtained results using LDA+Gutzwiller are in better agreement with existing experiments, suggesting significant improvements over LDA or LDA+ U .

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I. INTRODUCTION

The density-functional theory (DFT) (Refs. 1 and 2) is very successful in solid-state physics and materials science. First-principles calculations based on this theory, using the local density approximation (LDA) or the generalized gradient approximation (GGA), have been well developed and widely accepted as a powerful theoretical tool for explaining and predicting ground-state properties and electronic structures of a large amount of materials such as simple metals and band insulators.³ However both the LDA and GGA fail when they are applied to strongly correlated electron systems, a very important class of materials in condensed-matter physics. These materials contain unfilled d or f shells such as cuprates, manganites, ruthenates, Fe pnictides, and plutonium as well as the heavy-fermion systems. In the last 20 years, many efforts have been made to improve the situation. New methods, such as LDA+ U ,⁴ self-interaction-corrected (SIC) LDA,⁵ and LDA plus dynamical mean-field (DMFT) theory,⁶ have been proposed to provide new computational tools for the quantitative study of the strongly correlated materials. Those methods are quite successful in many aspects. Nevertheless a method that is practically efficient and can capture the key feature of the correlation effect as well is still absent for the ground-state studies.

One of the main features in correlated electron systems is that although the electrons in those narrow $3d$ or $4f$ bands are delocalized, they still show some atomic features, which are manifested in the appearance of the Hubbard band and the enhancement of the effective mass. In weakly correlated electron systems, electron states are delocalized in real space, exhibiting nearly-free-electron behavior which leads to good energy band description. The delocalization feature grants suitable electron-density-dependent forms for correlation energy as presented in LDA and GGA since the electron distribution is not far from homogeneous electron gas. However, if electrons exhibit strong localization feature of the atomic

orbitals, it is better to describe the electron states in real space. The presence of strong on-site correlations requires proper treatment of atomic configurations, which is orbital dependent and plays important roles in determining the physical property in this case. Methods such as LDA+ U (Ref. 4) and LDA+DMFT (Ref. 6) are proposed as remedies since this orbital-dependent feature is absent in both LDA and GGA. These methods start from similar Hamiltonians including on-site correlations but operate in different ways.

In LDA+ U method, the on-site interaction is treated in a static Hartree mean-field manner. It is suited for strongly correlated systems with long-range ordering, such as the antiferromagnetic (AF) ordered insulators, but it fails for intermediately correlated metallic systems. In DMFT method, the self-energy which is purely local in space is obtained in a self-consistent way, which makes the LDA+DMFT method the most accurate and reliable method now. However, the frequency-dependent feature of the self-energy makes it very time consuming, and the full charge-density self-consistency, which is very important for the accurate total-energy calculation, is hard to achieve.

Looking back to the progress of analytical treatment of strongly correlated system, we can notice that the Gutzwiller variational approach (GVA) has been proved to be quite efficient and accurate⁷⁻⁹ for the ground-state studies of many important phenomena, i.e., the Mott transition, ferromagnetism, and superconductivity. This approach was first introduced by Gutzwiller¹⁰ to study the itinerant ferromagnetism in systems with partially filled d bands described by the Hubbard model. In this approach, a many-body trial wave function was proposed, in which the weights of unfavorable atomic configurations are reduced according to the variational parameters. Both itinerant and atomic features can be described spontaneously by this type of wave function. Thus, a unified description from weakly to strongly correlated system can be built up by the GVA; this grants its capability to accurately capture the essence of correlated systems. Various

techniques have been developed to formulate this approach^{7,11–14} for different model Hamiltonians. The reliability and feasibility of GVA applied to correlated systems have been demonstrated by these theoretical studies.

In this paper, we will show that the GVA can be naturally combined with the DFT. As the result, the LDA+Gutzwiller (simply called LDA+G hereafter) method¹⁵ is proposed for practical calculations of correlated electron systems. To understand the formalism, we will show that a generalized Gutzwiller density-functional theory (GDFT) can be established following the same spirit of Kohn-Sham (KS) formalism in the DFT. The GDFT itself is rigorous; however, its exchange-correlation functional is unknown. By introducing certain approximation to the exchange-correlation energy in GDFT, the LDA+G method can be derived, very similarly as with the LDA or LDA+ U methods derived by approximation to the exchange-correlation term in the KS formalism. In order to show the validity and the advantage of this method, we will demonstrate that GVA is as accurate as DMFT for the ground-state properties, but computationally much cheaper. In addition, the present method is fully variational, which guarantees that many of the important physical quantities, such as the force or the linear response, can be naturally obtained from the variational principle. Detailed formalism of this method will be explicitly discussed here, and we will also show that a fully charge-density self-consistent procedure can be carried out, which is quite crucial for the total-energy calculations. Furthermore we will also show that LDA+G method is easy to be implemented into the existing codes, particularly if the LDA+ U method is already available.

This paper is organized as follows. In Sec. II, GVA is discussed for a multiband tight-binding Hamiltonian. Then we make detailed comparison between GVA and DMFT results in Sec. III. The combination of GVA with DFT and its derivation from GDFT will be presented in Sec. IV. In Sec. V, we apply the method to several typical systems and the results will be discussed. The proofs of some equations are put in the Appendix.

II. GUTZWILLER VARIATIONAL APPROACH

We start with the GVA for the ground state of correlated electron model systems. The detailed description of GVA has been presented by many authors; here we refer to Ref. 7 for the review. For generality, we consider a model system with a set of localized orbitals, such as d or f electrons, which can be described quite generally by the multiband Hubbard model. The Hamiltonian reads¹⁴

$$H = H_0 + H_{\text{int}} = \sum_{i,j;\sigma,\sigma'} t_{ij}^{\sigma,\sigma'} C_{i\sigma}^\dagger C_{j\sigma'} + \sum_i H_i \quad (1)$$

and

$$H_i = \sum_{\sigma,\sigma'(\sigma \neq \sigma')} U_i^{\sigma,\sigma'} \hat{n}_{i\sigma} \hat{n}_{i\sigma'}, \quad (2)$$

where σ is combined spin-orbit index of localized orbital basis $\{\phi_\sigma\}$ on site i : $\sigma=1, \dots, 2N$ (N is orbital number; e.g.,

$N=5$ for d electrons). The first part is just a tight-binding Hamiltonian extracted from LDA calculation, and the second term is the local atomic on-site interaction in which only density-density correlations are taken into account for simplicity. For generalized on-site interactions, please refer to Ref. 14.

We first examine the Hamiltonian in atomic limit (i.e., considering only the H_i term for single site). There are $2N$ different spin orbitals and each spin orbital could be either empty or occupied; thus there are totally 2^{2N} number of multi-orbital configurations $|\Gamma\rangle$. H_i is diagonal in the space cast by all $|\Gamma\rangle$ configurations since the on-site interactions are density-density type,

$$E_{i\Gamma} = \langle \Gamma | H_i | \Gamma \rangle = \sum_{\sigma,\sigma' \in \Gamma} U_i^{\sigma,\sigma'}. \quad (3)$$

$E_{i\Gamma}$ is the interaction energy of configuration $|\Gamma\rangle$ for the i th site. (For general interactions, the atomic part should be diagonalized, and the eigenvectors are linear combinations of $|\Gamma\rangle$.) Of course those possible configurations should not be equally weighted, and electrons tend to occupy those configurations which have relatively lower energy. For this purpose, we could construct projectors which project onto specified configurations $|\Gamma\rangle$ on site i ,

$$\hat{m}_{i\Gamma} = |i, \Gamma\rangle \langle i, \Gamma|, \quad (4)$$

with the normalization condition

$$\sum_{\Gamma} \hat{m}_{i\Gamma} = 1, \quad (5)$$

since all the configurations $\{|\Gamma\rangle\}$ form a locally complete set of basis.

In Eq. (1), if the interactions are not presented, the ground state is exactly given by the Hartree uncorrelated wave function (HWF) $|\Psi_0\rangle$, which is a single determinant of single-particle wave functions. However, after turning on the interaction terms, the HWF is no longer a good approximation since there are many energetically unfavorable configurations. In a physical view, to describe the ground state better, the weights of those unfavorable configurations should be suppressed. This is the main idea of Gutzwiller wave functions (GWFs). GWF $|\Psi_G\rangle$ is constructed by acting a many-particle projection operator on the uncorrelated HWF,

$$|\Psi_G\rangle = \hat{\mathcal{P}} |\Psi_0\rangle,$$

$$\hat{\mathcal{P}} = \prod_i \hat{\mathcal{P}}_i = \prod_i \sum_{\Gamma} \lambda_{i\Gamma} \hat{m}_{i\Gamma}. \quad (6)$$

The role of projection operator $\hat{\mathcal{P}}$ is to adjust the weight of each configuration through variational parameters $\lambda_{i\Gamma}$ ($0 \leq \lambda_{i\Gamma} \leq 1$). The GWF falls back to noninteracting HWF if all $\lambda_{i\Gamma}=1$. On the other hand, if $\lambda_{i\Gamma}=0$, the configuration Γ on site i will be totally removed. In this way, both the itinerant behavior of uncorrelated wave functions and the localized behavior of atomic configurations can be described consistently, and the GWF will give a more reasonable physical picture of correlated systems than HWF does.

The evaluation of GWF is a difficult task due to its many-body nature. There are many efforts in the literature, and the most famous one is Gutzwiller approximation (GA), introduced by Gutzwiller¹⁰ along with his proposal of GWF. In this approximation, the intersite correlation effect has been neglected and the physics meaning was discussed in Refs. 7 and 16. The exact evaluations of the single-band GWF in one dimension¹² and in the limit of infinite dimensions¹³ were carried out. It turns out that Gutzwiller approximation is exact in the latter case. Extensions to multiband correlated systems using Gutzwiller approximation were carried out by Bünemann *et al.*¹⁴ Meanwhile Gutzwiller approximation was proved to be equivalent to slave-boson theories^{17–19} on a mean-field level for both one-band case²⁰ and multiband case.^{21,22}

The expectation value of Hamiltonian (1) in GWF is

$$\langle H \rangle_G = \frac{\langle \Psi_G | H | \Psi_G \rangle}{\langle \Psi_G | \Psi_G \rangle} = \frac{\langle \Psi_0 | \hat{\mathcal{P}} H \hat{\mathcal{P}} | \Psi_0 \rangle}{\langle \Psi_0 | \hat{\mathcal{P}}^2 | \Psi_0 \rangle}. \quad (7)$$

Using the Gutzwiller approximation, in the limit of infinite dimensions, according to Ref. 14 we have

$$\langle H \rangle_G = \sum_{i \neq j; \sigma, \sigma'} t_{i,j}^{\sigma, \sigma'} z_{i\sigma} z_{j\sigma'} \langle C_{i\sigma}^\dagger C_{j\sigma'} \rangle_0 + \sum_{i; \sigma} \epsilon_{i\sigma} n_{i\sigma}^0 + \sum_{i; \Gamma} E_{i\Gamma} m_{i\Gamma}, \quad (8)$$

where $m_{i\Gamma}$ is the weight of configuration Γ ,

$$m_{i\Gamma} = \langle \Psi_G | \hat{m}_{i\Gamma} | \Psi_G \rangle \quad (9)$$

and

$$z_{i\sigma} = \sum_{\Gamma, \Gamma'} \frac{\sqrt{m_{\Gamma} m_{\Gamma'}} D_{\Gamma, \Gamma'}^\sigma}{\sqrt{n_{i\sigma}^0 (1 - n_{i\sigma}^0)}}, \quad (10)$$

with $D_{\Gamma, \Gamma'}^\sigma = |\langle \Gamma' | C_{i\sigma}^\dagger | \Gamma \rangle|$ and $0 \leq z_{i\sigma} \leq 1$. (See the Appendix for details.)

In order to understand the above Gutzwiller results properly, it is better to compare them with the Hartree-Fock scheme. For this purpose, here we give the Hartree-Fock expectation value of Hamiltonian (1) using HWF $|\Psi_0\rangle$,

$$\langle H \rangle_0 = \sum_{i \neq j; \sigma, \sigma'} t_{i,j}^{\sigma, \sigma'} \langle C_{i\sigma}^\dagger C_{j\sigma'} \rangle_0 + \sum_{i; \sigma} (\epsilon_{i\sigma} + \Delta \epsilon_{i\sigma}) n_{i\sigma}^0 + C, \quad (11)$$

where C is a constant and $\Delta \epsilon_{i\sigma}$, which is proportional to interaction strength U , is a correction to the on-site energy (level shift) introduced by the static mean-field treatment of the interaction term.

Comparing Eq. (8) with Eq. (11), now it is clear that the main differences between the Gutzwiller and the Hartree approaches are as follows:

(1) There are orbital-related factors $z_{i\sigma}$ in the former associated with the hopping terms, which describe the renormalization of kinetic energy, while the kinetic energy in the Hartree approach is not renormalized.

(2) The interaction energy in the Gutzwiller approach is not simply scaled with the interaction strength U , but it is

related to the configuration weights, while in the Hartree approach, the presence of interaction term will contribute simply to the on-site energy correction in proportional to U after the mean-field treatment.

The total energy under the GWF can be obtained by minimizing Eq. (8) with respect to configuration weights $m_{i\Gamma}$, which now in fact are variational parameters. Since more variational parameters are presented in this approach, the obtained ground-state total energy is much better than that in HWF. In other words, by using the GWF, the obtained ground-state total energy is further reduced due to the reduction in interaction energy, but in the cost of kinetic energy. The balance of the two (*gain* and *cost*) is achieved by the energy minimization with respect to variational parameters.

For the convenience of our following discussions, here we would like to generalize the formalism and make several definitions. Any operator \hat{A} acting on the GWF can be mapped to a corresponding Gutzwiller effective operator \hat{A}^G which acts on the HWF (rather than GWF), requiring that its expectation values are kept the same,

$$\langle \Psi_G | \hat{A} | \Psi_G \rangle = \langle \Psi_0 | \hat{\mathcal{P}}^\dagger \hat{A} \hat{\mathcal{P}} | \Psi_0 \rangle = \langle \Psi_0 | \hat{A}^G | \Psi_0 \rangle. \quad (12)$$

Here we have

$$A^G = \hat{\mathcal{P}}^\dagger A \hat{\mathcal{P}}. \quad (13)$$

If the operator \hat{A} is a single-particle operator, such as $\hat{A}_0 = \sum_{ij, \sigma\sigma'} A_{ij}^{\sigma\sigma'} C_{i\sigma}^\dagger C_{j\sigma'}$ (where $A_{ij}^{\sigma\sigma'} = \langle i\sigma | \hat{A}_0 | j\sigma' \rangle$), then similar to the above procedure for the evaluation of kinetic energy in Eq. (8), its Gutzwiller effective operator (in Gutzwiller approximation) can be written as

$$\hat{A}_0^G = \sum_{ij; \sigma\sigma'} A_{ij}^{\sigma\sigma'} z_{i\sigma} z_{j\sigma'} C_{i\sigma}^\dagger C_{j\sigma'} + \sum_{i; \sigma} (1 - z_{i\sigma}^2) C_{i\sigma}^\dagger C_{i\sigma} A_{ii}^{\sigma\sigma}, \quad (14)$$

where again $z_{i\sigma}$ are orbital-dependent renormalization factors, which are determined through the configuration weights presented in the projector $\hat{\mathcal{P}}$. Here please note that the diagonal term and the hopping term should be treated separately (see the Appendix).

Following the above general definition, we can now define a Gutzwiller effective Hamiltonian H^G which acts on HWF,

$$H^G = H_0^G + H_{\text{int}}^G, \quad (15)$$

such that the following equation holds:

$$\langle \Psi_0 | H^G | \Psi_0 \rangle = \langle \Psi_G | H | \Psi_G \rangle = E_G. \quad (16)$$

Here the kinetic part H_0^G can be written out according to Eq. (14), and the interaction part is

$$H_{\text{int}}^G = \sum_{i; \Gamma} E_{i\Gamma} \hat{m}_{i\Gamma} \quad (17)$$

for the density-density-type interaction as discussed above.

Now we are coming to a stage that we can solve the Gutzwiller problem easily through energy minimization. In practice, the minimization procedure will be done iteratively

with each loop being divided into two steps. The first step is to fix the Gutzwiller variational parameters m_Γ and find the optimal HWF. As we know the H^G for given m_Γ , which is noninteracting, this step can be easily done by diagonalizing H^G and filling the corresponding bands up to the Fermi level. Then in the next step, we will fix the HWF and optimize the energy respect to all the Gutzwiller variational parameters m_Γ . The explicit equation can be written as

$$\frac{\partial E_G}{\partial m_{i,\Gamma}} = \sum_{j,j \neq i} \left[\sum_{\sigma,\sigma'} t_{i,j}^{\sigma,\sigma'} \frac{\partial z_{i,\sigma}}{\partial m_{i,\Gamma}} z_{j,\sigma'} \langle C_{i\sigma}^\dagger C_{j\sigma'} \rangle_0 + \sum_{\sigma,\sigma'} t_{j,i}^{\sigma,\sigma'} z_{j,\sigma'} \frac{\partial z_{i,\sigma'}}{\partial m_{i,\Gamma}} \langle C_{j\sigma'}^\dagger C_{i\sigma} \rangle_0 \right] + E_{i\Gamma} = 0. \quad (18)$$

In this second step of calculations, for the lattice model with crystal periodicity, usually additional constraints can be adopted: (1) there is no site dependency for $z_{i\sigma}$ factors and occupation number $n_{i\sigma}$, i.e., $z_{i\sigma} = z_{j\sigma}$ and $n_{i\sigma} = n_{j\sigma}$; and (2) the charge on each orbital should be kept to be the same as that obtained by HWF (for pure density-density interaction as discussed in Ref. 14). In other words we have

$$\sum_{\Gamma} \langle \Gamma | C_{i\sigma}^\dagger C_{i\sigma} | \Gamma \rangle m_{i,\Gamma} = n_{i\sigma} = n_{i\sigma}^0 = \langle \hat{n} \rangle_0. \quad (19)$$

When all $m_{i\Gamma}$ are obtained, go back the first step to construct a new effective Gutzwiller Hamiltonian again. By this recursive method, all parameters $m_{i\Gamma}$ and $|\Psi_0\rangle$ can be obtained self-consistently.

Typically, the second step of variations, i.e., the optimization of $m_{i\Gamma}$, is not so easy for multiband systems because a large number of nonlinear equations need to be solved spontaneously. Fortunately, following the steps described in our previous paper,²³ we are able to transfer the nonlinear equations into linear equation set, and furthermore a so-called adiabatic solution searching procedure can be adopted. Those techniques will greatly reduce the computational cost and stabilize the calculations.

III. COMPARISON OF GUTZWILLER APPROXIMATION WITH DYNAMICAL MEAN-FIELD THEORY

In this section, we will compare the results obtained by the GVA and that by the DMFT for the single- and two-band Hubbard models. With the careful comparison of kinetic energies, interaction energies, and quasiparticle spectra, we are going to clarify the following important issue: can GA capture the important ‘‘incoherent motion’’ of the correlated electrons or not? This problem is considered to be the biggest shortcoming of GA, which prevents it to be widely used in the first-principles calculations of strongly correlated materials. As we will show below, the GA can definitely capture the effect of incoherent motion in the ground state by its multi-configuration nature, which leads to very good agreement with the DMFT ground-state results for both the kinetic and interaction energies. On the other hand the situation is not as good for the excited states since the variational parameters in the GA are determined by optimizing only the ground-state energy, not that of excited states. Therefore, GA is a much

better approximation for the ground state than for excited states. Within the frame of GA, it is difficult to construct the high-energy excited states corresponding to the upper and lower Hubbard bands. That is why in the Green’s function obtained by GA, we only have quasiparticle part and no Hubbard bands, while the problem only exists for the high-energy excited states and not for the ground state and the low-energy quasiparticle states.

We start from the multiband Hubbard model (1). For the clarity we only keep the intraorbital hopping $t_{i,j}^{\sigma,\sigma'} = t_{i,j} \delta_{\sigma,\sigma'}$ and neglect the on-site energy $\epsilon_{i,\sigma}$ in the following (restoring them does not change the conclusions). To describe quasiparticle states, an important physical quantity is Z factor. Actually, there are two different definitions of Z in literature. The first one is the renormalization factor of the effective bandwidth for the quasiparticles; the second one is the weight of the coherent part in the electron Green’s function near Fermi surface. As we will show below, in GA the Z factors obtained by the above two definitions match each other, while in DMFT they are quite different. In the following comparison, we compute Z within DMFT by $Z = (1 - \frac{\partial \text{Re} \Sigma^R}{\partial \omega} |_{\omega=0})^{-1}$, which is quasiparticle weight, while in GA calculation we define $Z = z^2$.

Under Gutzwiller approximation, the quasiparticle states and quasihole states can be expressed as²⁴

$$|\Phi_{k\sigma}^{p/h}\rangle = \begin{cases} \hat{P} C_{k\sigma}^\dagger |\Psi_0\rangle & \text{for } \epsilon_{k\sigma} > \mu_F \\ \hat{P} C_{k\sigma} |\Psi_0\rangle & \text{for } \epsilon_{k\sigma} < \mu_F. \end{cases}$$

With the above trial wave function, the excitation energy can be calculated as

$$\pm E_{k\sigma}^{p/h} = \frac{\langle \Phi_{k\sigma}^{p/h} | H | \Phi_{k\sigma}^{p/h} \rangle}{\langle \Phi_{k\sigma}^{p/h} | \Phi_{k\sigma}^{p/h} \rangle} - E_G \quad (20)$$

for quasiparticle (quasihole) excitations. The above equation can be evaluated by GA as shown in the Appendix, which leads to a simple expression of Green’s function,

$$G_{k\sigma}^{\text{coh}}(i\omega) = \frac{\gamma_{k\sigma}^2}{i\omega - z_{k\sigma}^2(\epsilon_{k\sigma} - \mu_F)},$$

with

$$\gamma_{k\sigma}^2 = \begin{cases} |\langle \Phi_{k\sigma}^p | C_{k\sigma}^\dagger | \Psi_G \rangle|^2 & \text{for } \epsilon_{k\sigma} > \mu_F \\ |\langle \Phi_{k\sigma}^h | C_{k\sigma} | \Psi_G \rangle|^2 & \text{for } \epsilon_{k\sigma} < \mu_F \end{cases}$$

being the weight of the coherent part spectrum, which can also be evaluated to be equal to z_σ^2 under GA as shown in the Appendix. Therefore within GA the quasiparticle weight is coincident with the renormalization factor of the kinetic energy; thus dynamical information is captured by variational approach.

In Figs. 1–4, we compare the kinetic energies, interaction energies, and Z factors from GA and DMFT calculations. We choose the noninteraction density of state to be $\rho(\epsilon) = \frac{2}{\pi D} \sqrt{D^2 - \epsilon^2}$, which corresponds to Bethe lattice with infinite connectivity. Anderson impurity model in DMFT is solved by Lanczos method, which gives essentially exact results. As could be seen in Figs. 1–4, GVA captures ground-state ener-

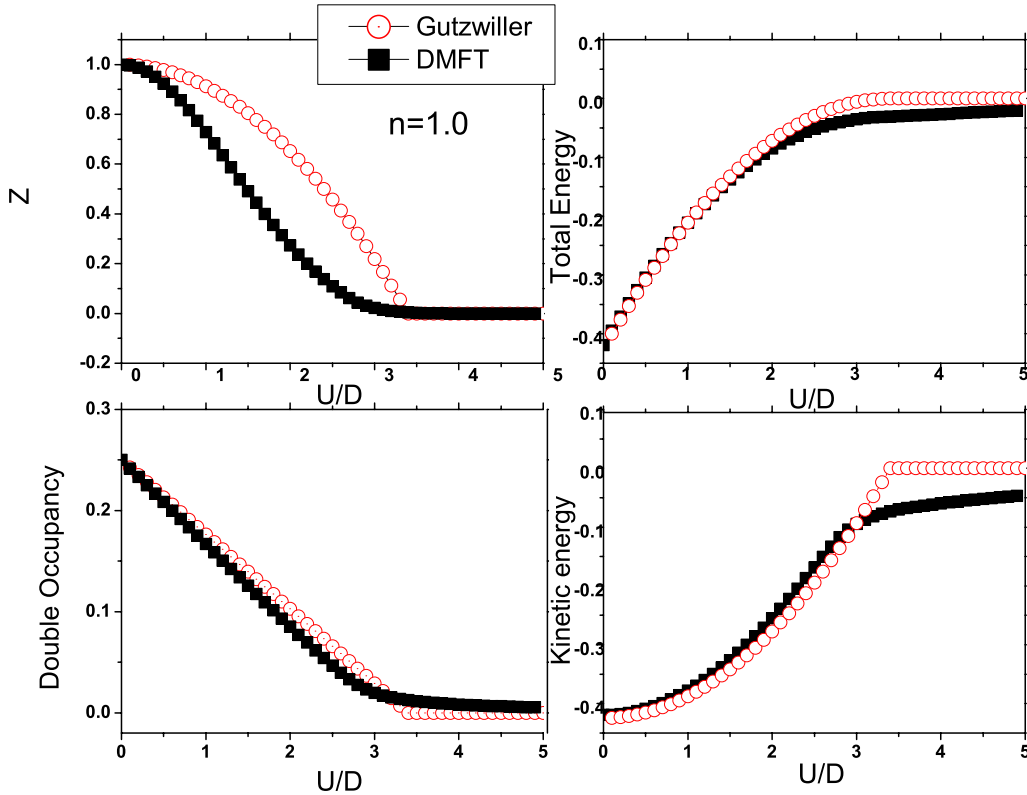


FIG. 1. (Color online) Comparisons of calculated Z factors, total energies, double occupancies, and kinetic energies of single-band Hubbard model with half filling. In GA the band renormalization factor and quasiparticle weight are coincident. Z factor from DMFT denotes quasiparticle weight. Double occupancy is $\langle n_{\uparrow}n_{\downarrow} \rangle$.

gies quite well for almost all correlation strengths and band fillings. Although as a variational approach it targets total energy and does not ensure the correctness of kinetic and interaction energies in principle, we still observe quite good coincidence of kinetic and interaction energies, respectively. We also notice that as the band degeneracy increases, there is further coincidence between GA and DMFT results as shown in Fig. 4 for two-band case.

For half filling $n=1.0$ where there is Mott insulator transition for large U , the introduction of GA further neglects spatial correlation and underestimates the absolute value of kinetic energy (Fig. 1). In Mott phase, GA gives vanishing double occupancy, while DMFT result always shows finite double occupancy due to spatial fluctuation. The flaw at large U could be traced back to the fact that the starting wave function of Gutzwiller projection is uncorrelated Fermi-liquid state $|\Psi_0\rangle$. This fact is also part of the reasons for the important shortcoming of GA: it miscaptures the high-energy excited states (seen from the overestimate of Z factor in Figs. 1–4 for large U). For all interaction strengths and band fillings, Z factor from GA is larger than that from DMFT treatment; i.e., the method gives more weight to low-energy coherent part. Nevertheless, we recently demonstrated²⁵ that this overestimation of Z factor can be further corrected by properly taking into account the contribution from excited states (namely, the incoherent motion of electrons).

To conclude this section, we make the assertion that as a cheap tool for correlated systems, GA has fairly good energy resolution, particularly good for the ground-state total energy

with dynamical information included. But care must be taken when dynamical information associated with high-energy excitations is tried to be extracted from the GA results.

IV. COMBINING DFT WITH GUTZWILLER VARIATIONAL APPROACH

In this section, we will discuss how we can combine the DFT with the GVA. The discussions will be separated into three parts. The detailed formalisms of LDA+G method are explicitly derived in the first part, which are used in realistic calculations. In the second part, we discuss a general GDFT, and then we derive the LDA+G formalism from the firm base of GDFT. In such a way, we demonstrate the rigidity of this method. Finally, in the third part, we will discuss the on-site interactions and the double-counting term.

A. Formalism of LDA+Gutzwiller method

As we discussed above, the strong on-site correlation is underestimated in LDA. For those strongly correlated materials, in which the correlations play very important roles in determine the electronic structure, this underestimation may lead to qualitative mistakes. One common procedure to overcome this problem is that we treat the interactions more explicitly on top of LDA level, just like what has been done in LDA+ U or LDA+DMFT schemes. The starting effective Hamiltonian is usually written as

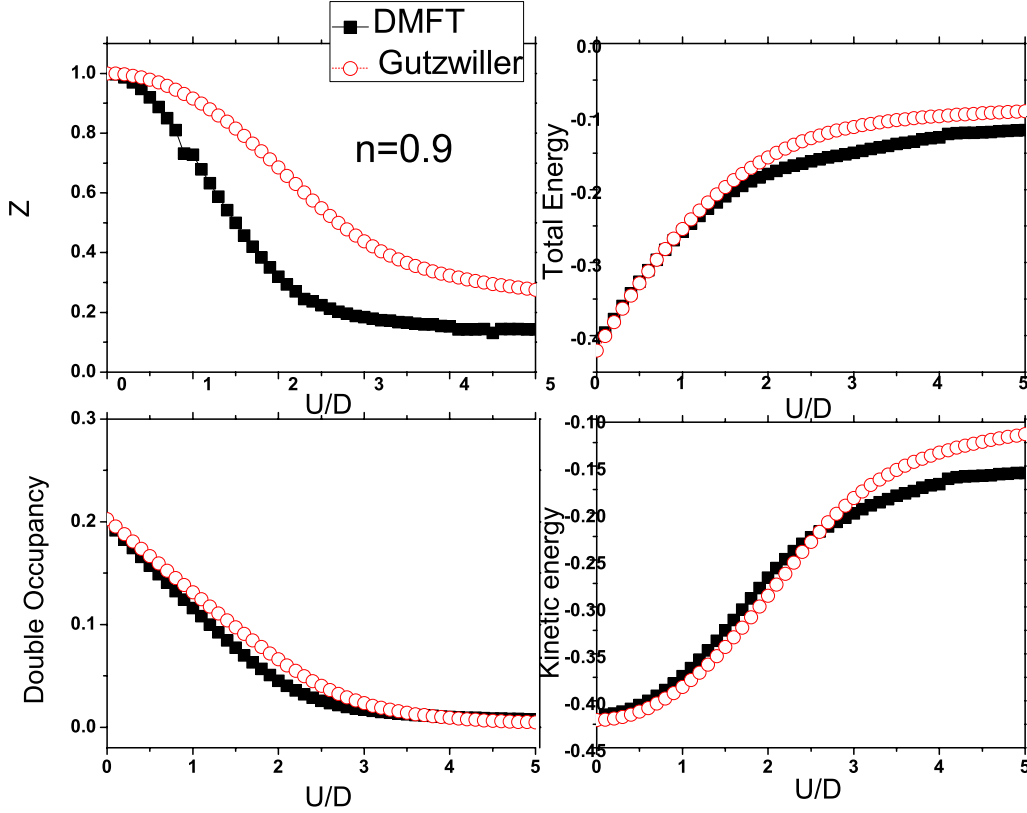


FIG. 2. (Color online) Comparisons of calculated Z factors, total energies, double occupancies, and kinetic energies of single-band Hubbard model with occupation number $n=0.9$.

$$H = H_{\text{LDA}} + H_{\text{int}} - H_{\text{dc}}, \quad (21)$$

where H_{LDA} is the LDA part Hamiltonian extracted from the standard LDA calculation, H_{int} is the on-site interaction term, and H_{dc} is the double-counting term representing the average orbital-independent interaction energy already included by LDA.

Both LDA+ U and LDA+DMFT methods start from the same Hamiltonian as shown above; however they treat the problem in different ways. In the LDA+ U scheme, Hartree-type mean-field approximation is used to solve the above Hamiltonian, which can capture the orbital-dependent physics (which is absent in LDA), but the dynamical correlation is still not included. On the other hand in the LDA+DMFT method, the purely local self-energy is evaluated by solving an effective quantum impurity model mapped from the original lattice model. With the frequency-dependent self-energy, not only the ground-state properties but also the dynamical response around the equilibrium can be considered by LDA+DMFT. Because of the frequency dependency of the self-energy, the LDA+DMFT is quite expensive in computational time. In many applications, we are only interested in the ground-state properties and it is quite important to develop a computational method for correlation materials, which is as fast as LDA+ U and can capture the dynamical correlation effect as well for the ground state.

As we have proposed in the previous paper,¹⁵ an alternative way to solve the problem is to use Gutzwiller wave function rather than single determinant Hartree wave func-

tion. This approach is much cheaper than DMFT, but its quality is as good as DMFT for the ground-state determination (as been shown in Sec. III) because it can capture the dynamical correlation effect due to the multiconfiguration nature of the Gutzwiller wave function. More importantly, this approach is fully variational, and can be easily combined with the DFT as will be discussed below.

Now the goal is to solve Hamiltonian (21) by the GVA. For this purpose, we need to discuss the Hamiltonian in more detail. Since the problem to be addressed here is generally orbital dependent, the effective Hamiltonian should be written in a set of complete orbital bases, which are always available, such as Wannier functions or atomic orbitals. These orbitals can be denoted by $|i\alpha\rangle$, in which i is site index, α is spin-orbital index, and $C_{i\alpha}^\dagger$ is the corresponding creation operator.

Following the basic idea of LDA+ U or LDA+DMFT approaches, the H_{LDA} term in effective Hamiltonian (21) is regarded as single-particle operator. It can be therefore expressed in terms of a complete set of orbitals as

$$H_{\text{LDA}} = \sum_{ij,\alpha\alpha'} t_{ij\alpha\alpha'} C_{i\alpha}^\dagger C_{j\alpha'},$$

$$t_{ij\alpha\alpha'} = \langle i\alpha | H_{\text{LDA}} | j\alpha' \rangle. \quad (22)$$

Suppose all the orbitals on the same site are correlated, and the interaction term can be written as

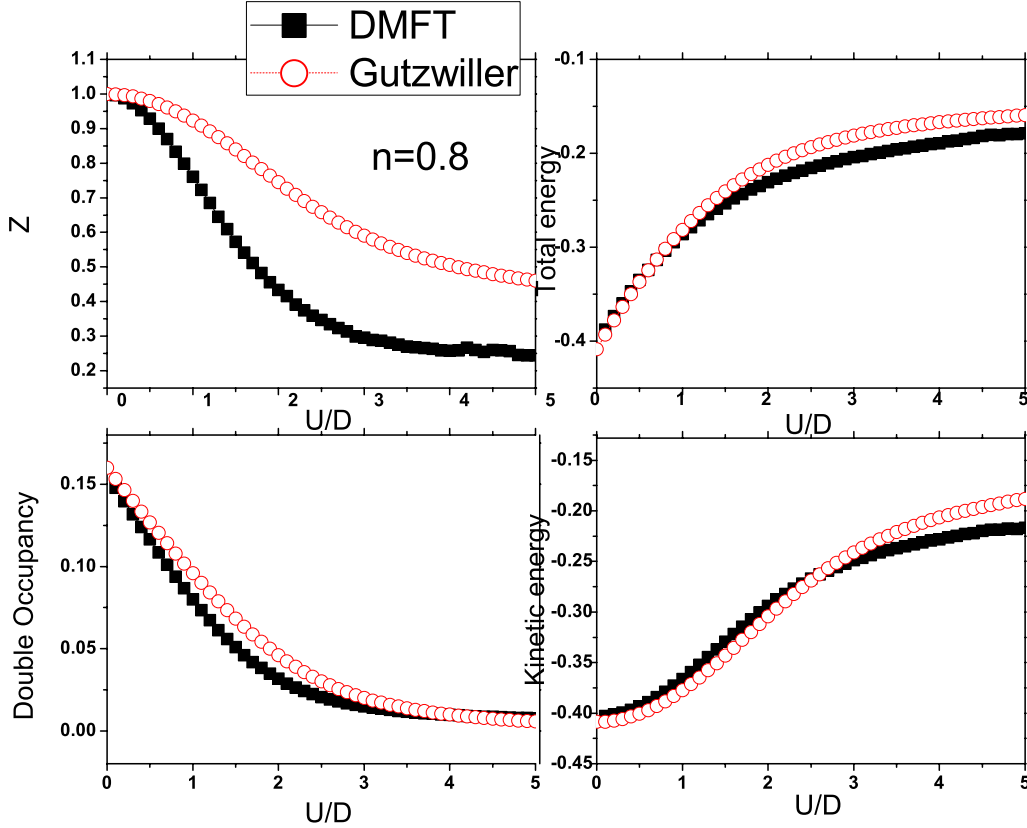


FIG. 3. (Color online) Comparisons of calculated Z factors, total energies, double occupancies, and kinetic energies of single-band Hubbard model with occupation number $n=0.8$.

$$H_{\text{int}} = \sum_{i\alpha\alpha'(\alpha\neq\alpha')} \mathcal{U}_i^{\alpha,\alpha'} \hat{n}_{i;\alpha} \hat{n}_{i;\alpha'}, \quad (23)$$

in which $\hat{n}_{i\alpha} = C_{i\alpha}^\dagger C_{i\alpha}$. Now it is easy to see that effective Hamiltonian (21) has the same form as that shown in Hamiltonian (1). (Please note the double-counting term only contributes to a constant uniform shift, and has no orbital dependency, as will be addressed in the latter part.) Then following the steps discussed in Sec. I, we will be able to solve the problem. This is the scheme used in most of post-LDA techniques, where a tight-binding fit to LDA results are first obtained, and then local orbital-dependent interaction terms are implemented and the problem with interaction should be solved by some many-body techniques. We can therefore call the above procedures as post-LDA plus Gutzwiller approaches, which has been recently used for several examples.^{26–28}

However, our intention is to develop a complete LDA +G method with full charge self-consistency and without tight-binding fitting. Two important factors have to be considered for this purpose. (1) Realistic materials consist of nonstrongly correlated bands, which can be treated nicely by LDA, and strongly correlated bands, which require the Gutzwiller step. Proper separation of two sets of energy bands is therefore necessary. (2) Full charge-density self-consistency need to be considered. These will be the main points for our following discussions.

We first divide the complete orbital basis into localized and extended orbitals, and the interactions are added only for localized orbitals, for example, d or f orbitals in transition-metal or rare-earth compounds. The localized and extended orbitals are labeled by $\{|i\sigma\rangle = C_{i\sigma}^\dagger|0\rangle\}$ and $\{|i\delta\rangle = C_{i\delta}^\dagger|0\rangle\}$, respectively, and the completeness of orbital basis requires that

$$\sum_{i\sigma} |i\sigma\rangle\langle i\sigma| + \sum_{i\delta} |i\delta\rangle\langle i\delta| = 1. \quad (24)$$

Under the representation of this basis set, the H_{LDA} reads

$$H_{\text{LDA}} = \left(\sum_{i\sigma} |i\sigma\rangle\langle i\sigma| + \sum_{i\delta} |i\delta\rangle\langle i\delta| \right) H_{\text{LDA}} \left(\sum_{j\sigma'} |j\sigma'\rangle\langle j\sigma'| + \sum_{j\delta'} |j\delta'\rangle\langle j\delta'| \right). \quad (25)$$

As discussed in Sec. I, the GWF $|\Psi_G\rangle$ is constructed from the HWF $|\Psi_0\rangle$ with proper projection. Any operator acting on GWF can be mapped to a Gutzwiller effective operator which acts on HWF instead. Since H_{LDA} only consists of single-particle operators, following the definition in Eq. (13), its corresponding Gutzwiller effective Hamiltonian can be written as

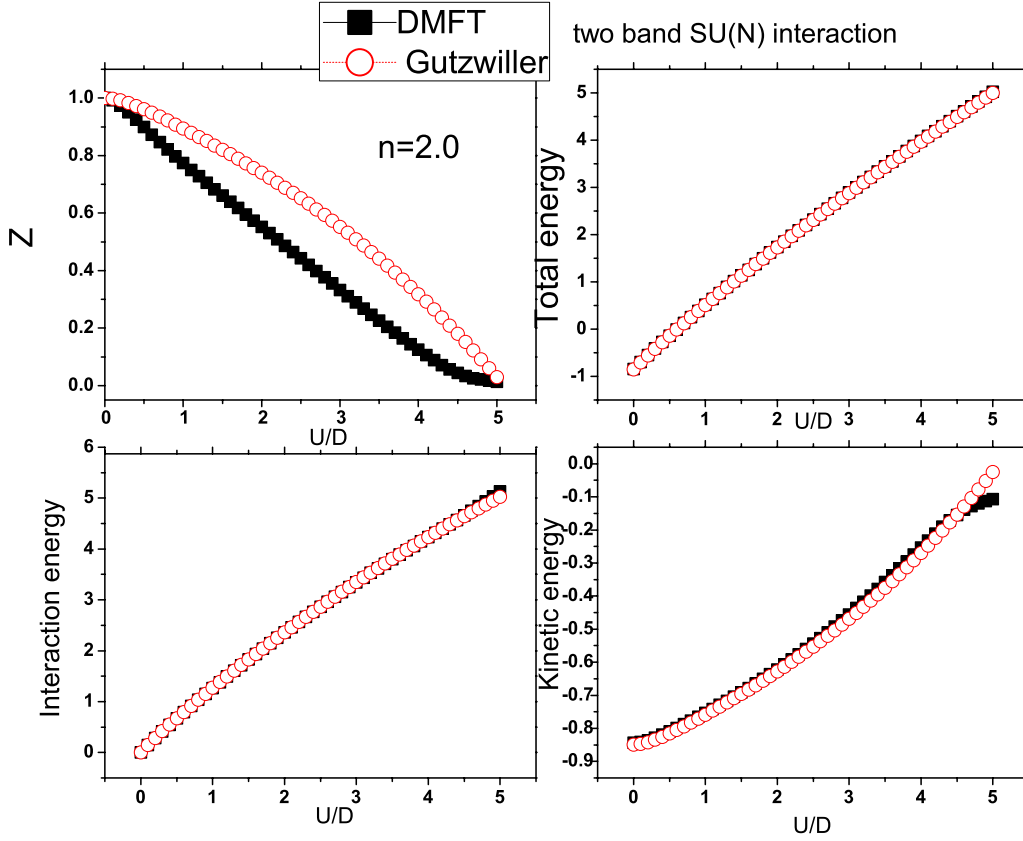


FIG. 4. (Color online) Comparisons of calculated Z factors, total energies, interaction energies, and kinetic energies of two-band Hubbard model with $SU(N)$ interaction.

$$\begin{aligned}
 H_{\text{LDA}}^G = & \left(\sum_{i\sigma} z_{i,\sigma} |i\sigma\rangle\langle i\sigma| + \sum_{i\delta} |i\delta\rangle\langle i\delta| \right) H_{\text{LDA}} \left(\sum_{j\sigma'} z_{j,\sigma'} |j\sigma'\rangle \right. \\
 & \times \langle j\sigma'| + \sum_{j\delta'} |j\delta'\rangle\langle j\delta'| \left. \right) + \sum_{i\sigma} (1 - z_{i\sigma}^2) |i\sigma\rangle \\
 & \times \langle i\sigma| H_{\text{LDA}} |i\sigma\rangle \langle i\sigma|. \quad (26)
 \end{aligned}$$

To derive this Gutzwiller effective Hamiltonian, it is essential to understand that for those noninteracting orbitals, the corresponding renormalization factor $z_{i\delta}$ is equal to 1. This formula could be further simplified using completeness condition (24),

$$\begin{aligned}
 H_{\text{LDA}}^G = & \left(\sum_{i\sigma} z_{i,\sigma} |i\sigma\rangle\langle i\sigma| + 1 - \sum_{i\sigma} |i\sigma\rangle\langle i\sigma| \right) H_{\text{LDA}} \left(\sum_{j\sigma'} z_{j,\sigma'} |j\sigma'\rangle \right. \\
 & \times \langle j\sigma'| + 1 - \sum_{j\sigma'} |j\sigma'\rangle\langle j\sigma'| \left. \right) + \sum_{i\sigma} (1 - z_{i\sigma}^2) |i\sigma\rangle \\
 & \times \langle i\sigma| H_{\text{LDA}} |i\sigma\rangle \langle i\sigma|, \quad (27)
 \end{aligned}$$

and the interaction energy is given as

$$\langle \Psi_G | H_{\text{int}} | \Psi_G \rangle = \sum_{i,\Gamma} E_{i,\Gamma} m_{i,\Gamma}. \quad (28)$$

Now it is clear that the complete basis set defined at beginning is actually not necessary for realistic calculations because only the localized orbitals $|i\sigma\rangle$ appear in the above equation. The interaction terms are also defined only for

those localized orbitals. We then come to a stage very similar to $\text{LDA}+U$, where localized orbitals are defined and interaction within those orbitals is supplemented. What is addition to $\text{LDA}+U$ scheme is that the kinetic energy of each local orbital is renormalized by factor $z_{i\sigma}$ which needs to be determined in terms of configuration weights and configuration energy through the variational approach as shown below.

In realistic calculations for solid crystals, it is more convenient to carry out the calculations in reciprocal space, especially for those plane-wave methods. The transformation to the reciprocal space is quite straightforward because the Gutzwiller approximation keeps the translational symmetry unbroken. We first define the Bloch states of localized orbitals $|i\sigma\rangle$,

$$|k\sigma\rangle = \frac{1}{N} \sum_i e^{ikR_i} |i\sigma\rangle. \quad (29)$$

Then the Gutzwiller effective Hamiltonian H_{LDA}^G in k space can be written as

$$\begin{aligned}
 H_{\text{LDA}}^G = & \left(\sum_{k\sigma} z_{\sigma} |k\sigma\rangle\langle k\sigma| + 1 - \sum_{k\sigma} |k\sigma\rangle\langle k\sigma| \right) H_{\text{LDA}} \\
 & \times \left(\sum_{k'\sigma'} z_{\sigma'} |k'\sigma'\rangle\langle k'\sigma'| + 1 - \sum_{k'\sigma'} |k'\sigma'\rangle\langle k'\sigma'| \right) \\
 & + \sum_{kk'\sigma} (1 - z_{\sigma}^2) |k\sigma\rangle\langle k'\sigma| H_{\text{LDA}} |k'\sigma\rangle\langle k\sigma|. \quad (30)
 \end{aligned}$$

Let us define the projector $\hat{P} = \sum_{k\sigma} \hat{P}_{k\sigma} = \sum_{k,\sigma} |k\sigma\rangle\langle k\sigma|$ which projects onto the Bloch state of localized orbital; then the projection to the remaining delocalized orbitals is taken into account by $1 - \hat{P}$. For convenience, here we also define another projector $\hat{Q} = \sum_{k,\sigma} z_{\sigma}^2 |k\sigma\rangle\langle k\sigma|$. Then we have

$$H_{\text{LDA}}^G = (1 - \hat{P} + \hat{Q})H_{\text{LDA}}(1 - \hat{P} + \hat{Q}) + \sum_{kk'\sigma} (1 - z_{\sigma}^2) |k\sigma\rangle \times \langle k'\sigma| H_{\text{LDA}} |k'\sigma\rangle \langle k\sigma|. \quad (31)$$

The total energy is obtained by evaluating the expectation value of the Hamiltonian,

$$E(\rho) = \langle \Psi_0 | H_{\text{LDA}}^G | \Psi_0 \rangle + \sum_{\Gamma} E_{\Gamma} m_{\Gamma} - E_{\text{dc}} \\ = \langle \Psi_0 | (1 - \hat{P} + \hat{Q}) H_{\text{LDA}} (1 - \hat{P} + \hat{Q}) | \Psi_0 \rangle \\ + \sum_{\sigma} (1 - z_{\sigma}^2) n_{\sigma} \mathcal{E}_{\text{LDA}}^{\sigma} + \sum_{\Gamma} E_{\Gamma} m_{\Gamma} - E_{\text{dc}}, \quad (32)$$

in which $\mathcal{E}_{\text{LDA}}^{\sigma} = \sum_k \langle k\sigma | H_{\text{LDA}} | k\sigma \rangle$, $n_{\sigma} = \sum_k \langle \Psi_0 | k\sigma \rangle \langle k\sigma | \Psi_0 \rangle$, and E_{dc} is the double-counting energy.

Now the remaining task is to minimize the total-energy functional with respect to variational parameters: uncorrelated wave function $|\Psi_0\rangle$ and atomic configuration weight m_{Γ} . Very similar to the familiar Kohn-Sham equation, the uncorrelated wave function $|\Psi_0\rangle$ in the periodic lattice can be written as a simple Slater determinant of single-particle wave functions $|\psi_{nk}\rangle$. Two sets of variational equations can be derived from minimization of Eq. (32) with respect to $|\psi_{nk}\rangle$ and m_{Γ} , respectively. For the variation with respect to $|\psi_{nk}\rangle$, please note that the orbital occupation number $n_{\sigma} = \sum_{nk} \langle \psi_{nk} | \hat{P}_{k\sigma} | \psi_{nk} \rangle$ also depends on $|\psi_{nk}\rangle$ inexplicitly,

$$\frac{\partial E(\rho)}{\partial f_{nk} \langle \psi_{nk} |} = \left[H_{\text{LDA}}^G + \frac{\partial E(\rho)}{\partial z_{\sigma}} \frac{\partial z_{\sigma}}{\partial n_{\sigma}} \hat{P}_{k\sigma} - H_{\text{dc}} \right] | \psi_{nk} \rangle = \epsilon_{nk} | \psi_{nk} \rangle, \quad (33)$$

$$\frac{\partial E(\rho)}{\partial m_{\Gamma}} = \sum_{\sigma} \frac{\partial E(\rho)}{\partial z_{\sigma}} \frac{\partial z_{\sigma}}{\partial m_{\Gamma}} + E_{\Gamma} = 0, \quad (34)$$

in which

$$\frac{\partial E(\rho)}{\partial z_{\sigma}} = \frac{2}{z_{\sigma}} \left(\frac{1}{2} \sum_{nk} f_{nk} \langle \psi_{nk} | \hat{P}_{k\sigma} H_{\text{LDA}}^G + H_{\text{LDA}}^G \hat{P}_{k\sigma} | \psi_{nk} \rangle - n_{\sigma} \mathcal{E}_{\text{LDA}}^{\sigma} \right). \quad (35)$$

When deriving this equation, the following relation is used:

$$z_{\sigma} \frac{\partial (1 - \hat{P} + \hat{Q})}{\partial z_{\sigma}} = z_{\sigma} | k\sigma \rangle \langle k\sigma | = (1 - \hat{P} + \hat{Q}) | k\sigma \rangle \langle k\sigma | \\ = (1 - \hat{P} + \hat{Q}) \hat{P}_{k\sigma}. \quad (36)$$

There are several constraints. The wave functions should be orthogonal and normalized, the total configuration weight must be unity, and for pure density correlations the local densities will not be changed in GVA:

$$\langle \psi_{nk} | \psi_{n'k'} \rangle = \delta_{n,n'} \delta_{k,k'},$$

$$\sum_{\Gamma} m_{\Gamma} = 1,$$

$$\sum_{\Gamma} \langle \Gamma | C_{\sigma}^{\dagger} C_{\sigma} | \Gamma \rangle m_{\Gamma} = \langle \hat{n}_{\sigma} \rangle_G = \langle \hat{n}_{\sigma} \rangle_0. \quad (37)$$

Through the above steps, we will be able to solve the problem for fixed LDA Hamiltonian H_{LDA} .

Now the question is how we can achieve self-consistency in the charge density. This step is very crucial, and the reason is the following: as we discussed above, all electrons (both delocalized and localized) should be included in realistic calculations. However those delocalized orbitals are treated in LDA level, and localized states are treated by the LDA+G step. The modification of the localized state will in return affect the charge distribution of all other delocalized states; particularly the charge transfer process between the delocalized and the localized orbitals may happen. This is of course important physics. If it is not treated properly, different conclusions may be drawn, as already discussed in the example studies for $\text{Na}_{1-x}\text{CoO}_2$,²⁹ where several post-LDA plus DMFT studies give different results.

The charge-density self-consistency can be achieved easily as long as the charge density can be constructed because the LDA Hamiltonian is determined by the electron density. In the present LDA+G scheme, the electron density can be constructed from the Gutzwiller wave functions by

$$\rho = \langle \Psi_G | \hat{\rho} | \Psi_G \rangle = \langle \Psi_0 | \hat{\rho}^G | \Psi_0 \rangle. \quad (38)$$

Since $\hat{\rho}$ is also a one-particle operator, similar to previous steps, with the help of Eq. (14) we have

$$\hat{\rho}^G = \left(\sum_{i\sigma} z_{i\sigma} |i\sigma\rangle \langle i\sigma| + 1 - \sum_{i\sigma} |i\sigma\rangle \langle i\sigma| \right) |r\rangle \langle r| \left(\sum_{j\sigma'} z_{j\sigma'} |j\sigma'\rangle \times \langle j\sigma'| + 1 - \sum_{j\sigma'} |j\sigma'\rangle \langle j\sigma'| \right) + \sum_{i\sigma} (1 - z_{i\sigma}^2) |i\sigma\rangle \langle i\sigma| |r\rangle \langle r| \\ \times |i\sigma\rangle \langle i\sigma|, \quad (39)$$

or we can write down the expression in the momentum space with the following simple expression:

$$\hat{\rho}^G = (1 - \hat{P} + \hat{Q}) |r\rangle \langle r| (1 - \hat{P} + \hat{Q}) + \sum_{kk'\sigma} (1 - z_{\sigma}^2) |k\sigma\rangle \langle k'\sigma| |r\rangle \\ \times \langle r| |k'\sigma\rangle \langle k\sigma|. \quad (40)$$

Equations (33) and (34) together with Eqs. (10) and (40) provide a self-consistent scheme, which is named LDA+Gutzwiller method by us. Equation (33) is similar to the KS equation in LDA or GGA, except that the Hamiltonian has been replaced by the corresponding effective Gutzwiller one with orbital-dependent terms. Equation (34), which is used to determine the configuration weight, and Eq. (10), which determines the factors z_{σ} , are given by GVA.

We illustrate our schematic self-consistent loops for LDA+G method in Fig. 5. Two main steps in this scheme are: (1) for fixed factor z_{σ} , solving the Kohn-Sham-type equation to get uncorrelated wave function Ψ_0 , and (2) for

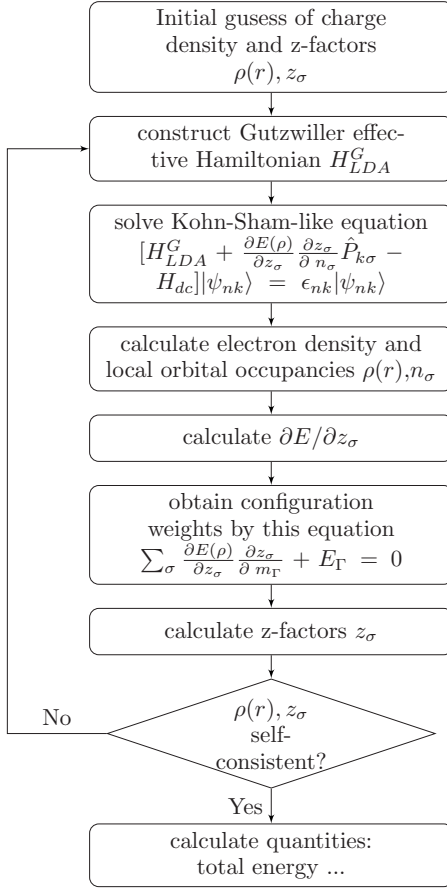


FIG. 5. Flow chart of self-consistent loops for LDA+Gutzwiller method.

fixed Ψ_0 , calculating the configuration weights m_Γ and then obtaining factor z_σ . The iteration loops end when both electron density and renormalization factors are self-consistent. This scheme could be easily implemented in all kinds of existing *ab initio* codes, no matter what kinds of basis sets are used for the wave function, because the essential computational requirement is just the calculations of projection to some local orbitals. If the LDA+ U method is already available in the original code, the implementation of LDA+G method will be much easier since the local orbitals defined in LDA+ U can be also used in the LDA+G formalism.

After the charge-density self-consistency has been achieved, the ground-state properties such as the stable crystal structure and magnetic structure as well as the elastic properties can be calculated, which is quite similar to the standard LDA procedure. Besides that, we can also obtain the density of states (DOS) by LDA+G. Because the band dispersion E_{nk} obtained by LDA+G is for the quasiparticle excitations, we can derive two types of DOSs from the LDA+G band structure. The first one is the quasiparticle DOS, which can be expressed as

$$\rho_{\text{QP}}(\omega) = \sum_{nk} \delta(\omega - E_{nk}). \quad (41)$$

Experimentally the electronic part of the low-temperature specific heat is directly determined by the quasiparticle DOS

and thus can be estimated by LDA+G for correlated materials. Another type of DOS is the integrated electronic spectral function, which is called electron DOS in LDA+G. Using z_σ obtained by the Gutzwiller approximation, the weight of the quasiparticle peak at E_{nk} appearing in the electronic spectral function can be expressed as

$$\mathcal{Z}_{nk} = \langle kn | \hat{Q}^2 | nk \rangle + \langle kn | 1 - \hat{P} | nk \rangle. \quad (42)$$

Then the electron DOS can be obtained by the summation over all k , which reads

$$\rho_{\text{el}}(\omega) = \sum_{nk} \mathcal{Z}_{nk} \delta(\omega - E_{nk}). \quad (43)$$

As we mentioned in Sec. III, only the coherent parts (quasiparticle peaks) can be captured by LDA+G and not the incoherent parts (Hubbard bands). The electron DOS in LDA+G corresponds to the low-energy part of the photoemission spectrum, which is mainly determined by the quasiparticle dynamics.

In the end, we would like to comment on the relationship between LDA+G method and LDA or LDA+ U . First it can be easily figured out that LDA+G method falls back to DFT-LDA method spontaneously in noncorrelated systems. This can be seen from the multiband Hubbard model in which on-site interactions go to zero; then no configuration is energetically unfavorable and GWF falls back to HWF. In LDA+G method, this case means that the supplemented on-site interaction energy and double-counting term are zero; then all localized orbitals are really delocalized and the corresponding renormalization parameters are $Z_\sigma=1$. The formalism falls back exactly to DFT-LDA.

LDA+Gutzwiller method can also cover the LDA+ U method when applied to strongly correlated insulators with long-range ordering, in which LDA fails while LDA+ U is successful. Actually this is quite easy to be understood. In the strongly correlated insulator with long-range ordering and integer occupation, such as the antiferromagnetic phase in the half-filled Hubbard model, the unit cell is doubled by the AF order, which greatly reduces the local fluctuation among the atomic configurations and thus increases the z factor to be close to unity. Again in the $z=1$ limit, the GWF returns back to HWF; the LDA+G energy functional is equivalent to that of LDA+ U when the z factors approach 1.

B. Derivation from Gutzwiller density-functional theory

In Sec. IV A, we have derived the LDA+G method in a physical but yet not rigorous way. In this section, however, we will derive the LDA+G method from a sound base. We will discuss a GDFT, which is rigorous and exact, just like the KS formalism developed from the DFT. In the KS formalism, as long as we know the functional of exchange-correlation energy $E_{\text{xc}}^{\text{KS}}$, we can solve the ground-state problem. This is also true for GDFT, where we have E_{xc}^{G} in its rigorous form instead of $E_{\text{xc}}^{\text{KS}}$. Of course, exact E_{xc}^{G} is unknown, and certain kinds of approximations have to be used in realistic calculations. In the KS formalism, if the LDA is used for the $E_{\text{xc}}^{\text{KS}}$ ($\approx E_{\text{xc}}^{\text{LDA}}$), then the LDA-KS-type formalism is realized. In addition, if LDA+ U approximation is used for

the E_{xc}^{KS} ($\approx E_{xc}^{LDA+U}$), the LDA+ U method can be obtained. We will show here that the LDA+ G method can be actually regarded as a “LDA+ U approximation in GDFT formalism,” where LDA+ U -type approximation is used for the exchange-correlation term. We will first establish the GDFT; then we derive the LDA+ G formalism from the firm base of GDFT.

1. DFT and Kohn-Sham

It is helpful to recall the basis of DFT first. The Hohenberg-Kohn (HK) theorem¹ shows that the total energy of an interacting electron system can be defined as a universal functional in terms of electron density $\rho(r)$. The ground-state energy is the global minimum of the functional. The electron density that minimizes the functional is the exact ground-state electron density. The equations are written as

$$E[\rho] = \langle \Psi | H | \Psi \rangle = T[\rho] + E_{\text{int}}[\rho],$$

$$\rho = \langle \Psi | \hat{\rho} | \Psi \rangle, \quad (44)$$

where $|\Psi\rangle$ is the ground-state many-body wave function, T is the kinetic energy, and E_{int} is the interaction energy. At this stage for simplicity, the energy due to external potential is not included in the formula (it will be supplemented later). This theorem is exact, but cannot be used directly since the explicit form of this functional is unknown. This problem can be transferred to an equivalent KS problem by using the well-known Kohn-Sham ansatz,² which is now become one of the most important basis of first-principles electronic structure calculations for solid states. In this ansatz, a reference system is introduced, whose exact Hamiltonian is still unknown, but we know that its ground-state wave function can be exactly written as the HFW $|\Psi_0\rangle$. (Therefore, the reference system here is actually a noninteracting system because we know that its wave function is $|\Psi_0\rangle$.) As long as the charge density of the reference system ρ^0 matches the true ground-state charge density (i.e., $\rho^0 = \rho$), then from the Hohenberg-Kohn DFT, the total energy of the true system can be reproduced through the reference system,

$$E[\rho] = E^{KS}[\rho^0] = T^{KS}[\rho^0] + E_H^{KS}[\rho^0] + E_{xc}^{KS}[\rho^0]$$

$$= \langle \Psi_0 | \hat{T} | \Psi_0 \rangle + E_H^{KS}[\rho^0] + E_{xc}^{KS}[\rho^0],$$

$$\rho = \rho^0 = \langle \Psi_0 | \hat{\rho} | \Psi_0 \rangle. \quad (45)$$

The KS kinetic energy T^{KS} and the Hartree energy E_H^{KS} of the reference system are different from the true kinetic and interaction energies, T and E_{int} , but importantly their functional forms are known. The KS idea is simply to reorganize the total-energy expression such that those known parts can be treated explicitly and all unknown parts are moved into the third term called exchange-correlation energy E_{xc}^{KS} . It is in this sense that KS formalism is still exact for the ground-state total energy. The merit of KS formalism is that the problem is solvable as long as the functional form E_{xc}^{KS} is known. By definition, the exchange-correlation energy is given as

$$E_{xc}^{KS} = \Delta T^{KS} + \Delta E_{\text{int}}^{KS} = (T - T^{KS}) + (E_{\text{int}} - E_H^{KS}), \quad (46)$$

where two contributions should be physically included: (1) the correction to the kinetic energy, ΔT^{KS} ; and (2) the correction to the interaction energy, $\Delta E_{\text{int}}^{KS}$.

The KS formalism up to now is exact. However certain kinds of approximations have to be made for E_{xc}^{KS} in realistic calculations, as will be discussed below. Nevertheless, here we want to put a note for the reference system. Once the approximation has been introduced for the exchange-correlation term E_{xc}^{KS} , the nature of the reference system may be modified. In reality, if the LDA+ U approximation is used for the exchange-correlation potential in KS formalism, the reference system is no longer noninteracting, and the $|\Psi_0\rangle$ is just an approximate wave function.

2. GDFT

Here we can establish an exact GDFT in parallel to KS formalism. One can see from KS formalism that taking a noninteracting system as reference is not a necessity. What is really important is to know the exact form of the wave function of the reference system, such as $|\Psi_0\rangle$ in KS. The main benefit of this strategy is that in the reference system the kinetic operator can be evaluated explicitly in quite a simple form. In the spirit of Kohn-Sham ansatz, any system can be taken as reference provided that it has the same electron density as the true system. We can theoretically formulate the exact GDFT, similar to KS, as follows:

(1) To replace the original difficult interacting many-body system, we choose an auxiliary reference system, whose exact Hamiltonian is still unknown, but we know that its ground-state wave function is given as the Gutzwiller wave function $|\Psi_G\rangle$ (rather than the HFW $|\Psi_0\rangle$). An important point to be noticed here is that the fact that whether the reference system is interacting or noninteracting actually does not matter since the Gutzwiller wave function can be used to describe both the interacting and noninteracting systems in a better way. (The nature of the reference system depends on the choice of exchange-correlation potential as will be further discussed in the following part.)

(2) Following the KS ansatz, we assume that the ground-state density of the original interacting system is equal to that of the reference system, $\rho^G = \rho$. (The representability is not rigorously proved at this stage; therefore this step is still an ansatz. However, considering the fact that the Ψ^G automatically returns back to Ψ_0 in the noninteracting limit, it has the same spirit as KS ansatz which has been proved to be valid for many applications.)

(3) The kinetic energy of the reference system can be explicitly written as $T^G = \langle \Psi_G | \hat{T} | \Psi_G \rangle$.

(4) All unknown parts are moved into the exchange-correlation energy E_{xc}^G . Finally, the total energy and the charge density will be written as

$$E[\rho] = E^G[\rho^G] = T^G[\rho^G] + E_H^G[\rho^G] + E_{xc}^G[\rho^G]$$

$$= \langle \Psi_G | \hat{T} | \Psi_G \rangle + E_H^G[\rho^G] + E_{xc}^G[\rho^G],$$

$$\rho = \rho^G = \langle \Psi^G | \hat{\rho} | \Psi^G \rangle. \quad (47)$$

The above formulation of GDFT is still exact, like KS. We can also come to the same conclusion as KS that if the exact exchange-correlation energy E_{xc}^G is known, the exact ground-state energy of the true system will be obtained. Again for the physical understanding, two terms are included in the exchange-correlation energy: (1) the correction to the kinetic energy ΔT^G ; and (2) the correction to the interaction energy, ΔE_{int}^G , expressed as

$$E_{xc}^G = \Delta T^G + \Delta E_{int}^G = (T - T^G) + (E_{int} - E_H^G). \quad (48)$$

As already mentioned, the Ψ_G automatically return back to Ψ_0 in the noninteracting limit; therefore the present GDFT can be regarded as a general extension of original KS formalism. The spirit of GDFT here is very similar to previously developed generalized Kohn-Sham (GKS) scheme³⁰ where an interacting reference system is chosen. However, GDFT is different from GKS in the following sense. In GDFT, we know that the wave function of the reference system is given as the Gutzwiller wave function. In GKS, on the other hand, the wave function of the reference system is still represented as a single Slater determinant, but the energy functional is modified to take into account the interacting energy explicitly.³⁰

3. Approximations for E_{xc}

Certain approximation has to be introduced for the unknown exchange-correlation part in order to perform practical calculations. We will start from the LDA and LDA+ U approximations used in KS formalism, and then we will show that by introducing the LDA+ U -type approximation into GDFT, the LDA+ G method can be derived.

a. LDA or GGA. The most popularly used and widely accepted approximation is the LDA, where the exchange-correlation energy is approximated as

$$E_{xc}^{KS} \approx E_{xc}^{LDA} = \Delta T^{LDA} + \Delta E_{int}^{LDA}. \quad (49)$$

We assume that the readers have the basic knowledge about LDA; we therefore do not discuss its details here. The only point we want to emphasize is that the LDA is basically parametrized from the uniform electron gas, so there are no localized orbitals in the LDA formalism and orbital-dependent terms are taken into account just like in a mean-field way as mentioned previously. This is the reason why LDA works well for simple metals, such as Na and K, where wide s band crosses the Fermi level, but it fails for strongly correlated systems, such as transition-metal oxides.

b. LDA+ U for strongly correlated systems. To overcome the problem of LDA for strongly correlated systems, LDA+ U method has been used, where the exchange-correlation energy is approximated as

$$\begin{aligned} E_{xc}^{KS} &\approx E_{xc}^{LDA+U} = \Delta T^{LDA} + \Delta E_{int}^{LDA+U} \\ &= \Delta T^{LDA} + \Delta E_{int}^{LDA} + \langle H_{int} \rangle_0 - E_{dc} \\ &= E_{xc}^{LDA} + \langle H_{int} \rangle_0 - E_{dc}. \end{aligned} \quad (50)$$

The spirit of LDA+ U method is that the LDA does not treat the interaction energy sufficiently well, and it needs to be

corrected for strongly correlated systems. Therefore, the interaction energy correction in original LDA ΔE_{int}^{LDA} is replaced by the LDA+ U counterpart, $\Delta E_{int}^{LDA+U} = \Delta E_{int}^{LDA} + \langle H_{int} \rangle_0 - E_{dc}$. In such a way, the interaction term is treated more explicitly, and the energy is improved.

To understand the LDA+ U formalism, it is very important to notice the following points: (1) The reference system (in KS) is no longer noninteracting anymore since the interaction term H_{int} is supplemented from the exchange-correlation potential. Therefore, the $|\Psi_0\rangle$ is no longer the rigorous eigenstate of the reference system; instead it is just an approximation. (2) It is only up to this step that the definition of local orbital and interaction strength U is necessary. In such a way, the orbital-dependent potential is given (the LDA-type E_{xc}^{LDA} only depends on the density, not on the orbital).

The LDA+ U method is quite successful for many of the insulating systems, which have AF long-range ordered ground state; however its quality is still not sufficient and can be improved further. The main drawbacks of LDA+ U are twofold: (1) the supplemented interacting term H_{int} is treated by crude Hartree scheme, and the interaction energy is typically overestimated. Actually, once the reference system becomes interacting system, the Ψ_0 is no longer a rigorous wave function. (2) Due to the usage of Ψ_0 as an approximate wave function, only the interaction energy is further corrected (over LDA); namely, $\langle H_{int} \rangle_0$ is the further correction to the interaction energy. But the kinetic part ΔT is still kept to be the same as that in LDA (ΔT^{LDA}). However it is known that the presence of interaction term should also renormalize the kinetic energy. Those drawbacks can be improved from our LDA+ G formalism as will be derived below.

4. Derivation of LDA+ G from the GDFT

The GDFT itself is also exact; however, certain approximations have to be used for the E_{xc}^G in practical calculations. Since the exchange-correlation energy is a functional of charge density, the easiest way of course is still to use the local density approximation, and neglect the nonlocal part of the potential, i.e., $E_{xc}^G \approx E_{xc}^{LDA}$. For the Hartree energy, it only depends on the charge density, and it is the same for both KS-DFT and GDFT, i.e., $E_H^G = E_H^{KS}$. Therefore, after applying the LDA to E_{xc}^G , all the potential energies in GDFT recover to be the same as that in LDA-KS. In this limit, we already know that the reference system is a noninteracting system, and the wave function Ψ_G should return back to Ψ_0 . Therefore, all the above GDFT formalism returns back to LDA-KS if the LDA is used for E_{xc}^G . So far, we gain nothing from the usage of GDFT. However, if the LDA+ U -type approximation is used for E_{xc}^G in GDFT, the situation will be much improved.

As have been discussed above, to overcome the problem of LDA for strongly correlated system, the strategy of LDA+ U approximation is to use a supplemented interaction term H_{int} in the exchange-correlation potential, such that the electron-electron (e-e) interaction can be treated more explic-

itly beyond LDA. The reference system now is no longer noninteracting, but Ψ_0 is still used to approximate the wave function of the reference system in the LDA+ U KS formalism. The same approximation for the exchange-correlation term can be also used in the GDFT; namely, an interaction term H_{int} can be supplemented in the exchange-correlation potential to describe the electrons in localized orbitals better (beyond uniform electron gas in LDA). Again, the reference system is an interacting system now; however, what is different in GDFT is that the wave function of reference system is given as Ψ_G rather than Ψ_0 . Of course, the GWF Ψ_G is much better than HWF Ψ_0 for interacting system, and it is in this sense that the formalism is improved over LDA+ U .

Therefore, using the similar LDA+ U approximation in the GDFT, exchange-correlation energy and the corresponding total energy can be written as

$$\begin{aligned} E[\rho] &= T^G[\rho] + E_H[\rho] + E_{\text{xc}}^G[\rho] \\ &= \langle \Psi_G | \hat{T} | \Psi_G \rangle + E_H[\rho] + E_{\text{xc}}^G[\rho], \\ E_{\text{xc}}^G &\approx E_{\text{xc}}^{\text{LDA}+\text{G}} = \Delta T^{\text{LDA}} + \Delta E_{\text{int}}^{\text{LDA}+\text{G}} \\ &= \Delta T^{\text{LDA}} + \Delta E_{\text{int}}^{\text{LDA}} + \langle H_{\text{int}} \rangle_G - E_{\text{dc}} \\ &= E_{\text{xc}}^{\text{LDA}} + \langle H_{\text{int}} \rangle_G - E_{\text{dc}}. \end{aligned} \quad (51)$$

It differs from the LDA+ U KS scheme in the following two points: (1) the supplemented interaction term is more precisely dealt with the Gutzwiller wave function; namely, the $\langle H_{\text{int}} \rangle_G$ is used instead of $\langle H_{\text{int}} \rangle_0$. (2) Although the ΔT^{LDA} is still used in the exchange-correlation functional, the kinetic energy is actually improved through the replacement of T^{KS} by T^G . The usage of ΔT^{LDA} in E_{xc}^G requires more discussions. It is known that the drawback of ΔT^{LDA} is that it keeps only the local part and neglects the nonlocal part. Therefore, to make improvement, nonlocal correction should be supplemented. However, it is seen from our above GDFT formalism that the nonlocal correction to the kinetic energy has been naturally included through the replacement of $\langle \Psi_0 | \hat{T} | \Psi_0 \rangle$ by $\langle \Psi_G | \hat{T} | \Psi_G \rangle$. Therefore, in the exchange-correlation part, the nonlocal correction to the kinetic energy is no longer necessary, and only local part needs to be considered. This is the reason why ΔT^{LDA} can be used for E_{xc}^G . The usage of ΔT^{LDA} in E_{xc}^G can also guarantee that the present LDA+G formalism returns back to the LDA+ U solution in the static limit, where the z factors approach unity and $|\Psi^G\rangle$ approach $|\Psi^0\rangle$.

Up to this stage, we have finished all the necessary steps, and we show that the original LDA+G formalism discussed in Sec. IV A can be derived from a more rigorous base, namely, the ‘‘LDA+ U -type approximation for the exchange-correlation potential in the exact GDFT formalism.’’ Using Eq. (51), Hamiltonian (21) discussed in Sec. IV A under GWF will be recovered. To be more practical, here we will write down the final version of the necessary equations explicitly. The total energy and the exchange-correlations read

$$E[\rho] = \langle \Psi_G | \hat{T} | \Psi_G \rangle + E_H[\rho] + \int V_{\text{ext}} \rho d^3r + E_{\text{xc}}^G[\rho],$$

$$E_{\text{xc}}^G \approx E_{\text{xc}}^{\text{LDA}+\text{G}} = E_{\text{xc}}^{\text{LDA}} + \langle \Psi_G | H_{\text{int}} | \Psi_G \rangle - E_{\text{dc}}, \quad (52)$$

in which the electron density now is

$$\rho(r) = \langle \Psi_G | r | \Psi_G \rangle = \langle \Psi_0 | \hat{\rho}^G | \Psi_0 \rangle \quad (53)$$

and the kinetic-energy operator is

$$T = \sum_i -\frac{1}{2} \nabla_i^2, \quad (54)$$

where i is electron label. The Hartree interaction energy of electrons is

$$E_H = \frac{1}{2} \int d^3r d^3r' \frac{\rho(r)\rho(r')}{|r-r'|}. \quad (55)$$

If the supplemented interaction part of the Hamiltonian is diagonal in configuration space (this is true if only density-density interactions are considered), the interaction term in the exchange-correlation energy reads according to Eqs. (2), (3), and (8) as

$$\langle \Psi_G | H_{\text{int}} | \Psi_G \rangle = \langle \Psi_G | \sum_i H_i | \Psi_G \rangle = \sum_{i;\Gamma} E_{i\Gamma} m_{i\Gamma}. \quad (56)$$

For convenience, external potential energy, Hartree energy, and exchange-correlation energy (of LDA part) can be grouped together, and written as a functional form of charge density,

$$E_{e\text{Hxc}}[\rho] = E_H[\rho] + \int V_{\text{ext}} \rho d^3r + E_{\text{xc}}^{\text{LDA}}[\rho], \quad (57)$$

and the effective potential is defined as

$$V_{e\text{Hxc}} = \frac{\delta E_{e\text{Hxc}}[\rho]}{\delta \rho}, \quad (58)$$

which is exactly the same as that in the LDA-KS formalism.

Now the total energy is

$$\begin{aligned} E[\rho, m_{i\Gamma}] &= \langle \Psi_G | T | \Psi_G \rangle + E_{e\text{Hxc}}[\rho] + \sum_{i;\Gamma} E_{i\Gamma} m_{i\Gamma} - E_{\text{dc}} \\ &= \langle \Psi_0 | T^G | \Psi_0 \rangle + E_{e\text{Hxc}}[\rho] + \sum_{i;\Gamma} E_{i\Gamma} m_{i\Gamma} - E_{\text{dc}}. \end{aligned} \quad (59)$$

The total energy is a functional of uncorrelated wave functions $|\Psi_0\rangle$ and the configuration weight $m_{i\Gamma}$, and has just the same form as Eq. (32). Both should be variationally optimized as already shown in Sec. IV A.

For a summary of this section, we have performed an explicit derivation just in the spirit of the Kohn-Sham ansatz to incorporate the Gutzwiller approach into density-functional theory. With some reasonable approximations, we prove that this scheme gives the same result as what we developed in Sec. IV A within a simple physical interpretation. This provides a reliable foundation of this LDA+G method.

C. Interaction and double-counting terms

Similar to all kinds of LDA+ U or LDA+DMFT calculations, the interaction and the double-counting terms remain

to be defined explicitly in the present LDA+G method. It is therefore also a kind of semiempirical *ab initio* method in this sense. Nevertheless, we can in general follow the same definition used in LDA+ U or LDA+DMFT method. From the physical point of view, we only consider the strong on-site interactions of localized orbitals. The interaction strength can be explicitly expressed with Slater integrals (or called Slater-Condon parameters) (F^0, F^2, \dots) in the atomic limit. However, in practice, it is more convenient to use ‘‘Kanamori parameters,’’ U, U', J , and J' , which are combinations of Slater integrals. The general form of the on-site interactions can be written as³¹

$$H_i = U \sum_{\alpha} n_{i\alpha\uparrow} n_{i\alpha\downarrow} + \frac{U'}{2} \sum_{\alpha \neq \alpha', \chi \chi'} n_{i\alpha\chi} n_{i\alpha'\chi'} - \frac{J}{2} \sum_{\alpha \neq \alpha', \chi} n_{i\alpha\chi} n_{i\alpha'\chi} - \frac{J}{2} \sum_{\alpha \neq \alpha', \chi} c_{i\alpha\chi}^{\dagger} c_{i\alpha\chi} c_{i\alpha'\chi}^{\dagger} c_{i\alpha'\chi} - \frac{J'}{2} \sum_{\alpha \neq \alpha'} c_{i\alpha\uparrow}^{\dagger} c_{i\alpha\downarrow}^{\dagger} c_{i\alpha'\uparrow} c_{i\alpha'\downarrow}, \quad (60)$$

where α denotes localized orbital and χ denotes spin. The first two terms are intraorbital Coulomb interaction and interorbital Coulomb interaction, respectively. The Hund rule exchange coupling is divided into three parts: one is the longitudinal part (the third term) which only involves density-density coupling; and the other two terms (the fourth and fifth terms) describe the spin-flip and pair-hopping processes, respectively. In the atomic case, the relation $U = U' + J + J'$ holds to retain the rotational invariance in orbital space. For typical d -orbital systems, where spin-orbital coupling is not so strong, the relation $J = J'$ also holds; we therefore have $U' = U - 2J$ in general.

In this paper, we restricted ourselves to the pure density-density interactions for simplicity, and the interactions to be considered are

$$H_i = U \sum_{\alpha} n_{i\alpha\uparrow} n_{i\alpha\downarrow} + \frac{U'}{2} \sum_{\alpha \neq \alpha', \chi \chi'} n_{i\alpha\chi} n_{i\alpha'\chi'} - \frac{J}{2} \sum_{\alpha \neq \alpha', \chi} n_{i\alpha\chi} n_{i\alpha'\chi}. \quad (61)$$

This on-site interaction Hamiltonian is already diagonal in the atomic configuration $|\Gamma\rangle$ space, and the corresponding configuration energy E_{Γ} is a linear combination of U, U' , and J .¹⁴

With the on-site interactions determined, we come to the question of how much of them are taken into account in LDA, that is, how to write down the double-counting terms. It is known that these interactions go into LDA in an average way without orbital dependence. As already discussed in LDA+ U or LDA+DMFT methods, we just follow the common choice of the double-counting terms as⁴

$$E_{\text{dc}}[n_i] = \sum_i \frac{\bar{U}}{2} n_i (n_i - 1) - \sum_i \frac{\bar{J}}{2} [n_{i\uparrow} (n_{i\uparrow} - 1) + n_{i\downarrow} (n_{i\downarrow} - 1)], \quad (62)$$

where n_i is the total electron number of localized orbitals on the same site i , $n_i = n_{i\uparrow} + n_{i\downarrow} = \sum_{\alpha\chi} n_{i\alpha\chi}$, and \bar{U} and \bar{J} are spheri-

cally averaged interactions, which can be given as⁶

$$\bar{U} = \frac{1}{(2l+1)} (U + 2lU'), \quad (63)$$

$$\bar{J} = \bar{U} - U' + J, \quad (64)$$

where l is the angular momentum number of the corresponding localized shell.

The Coulomb and exchange interactions, U and J , can in principle be obtained using corresponding Slater integrals. However, in real materials, the bare electron-electron interactions must be screened, and the Slater integrals have to be renormalized. Therefore, it is a hard task to determine the effective U and J exactly. In practice, usually two possible ways are followed: (1) determining the parameters from available experimental information empirically; and (2) calculating the parameters from constrained LDA method⁴ and the linear-response approach.³² Depending on different methods, different values might be obtained; however the important strategy is that for single fixed parameter, the method should be able to explain all possible properties spontaneously and systematically, rather than using different parameters for different properties. It is only in this way that the obtained results can be justified. We should also notice that the interaction parameters also depend on the choice of local orbitals because of the different screening processes involved. For example, both atomic orbitals and Wannier functions can be used to define the local orbitals. However generally the effective interaction strength for atomic orbitals should be larger than that for Wannier orbitals because the former is more localized. To construct the Wannier orbitals, either the projected Wannier method³³ or the maximally localized Wannier function³⁴ can be used.

Finally, a very similar approach was recently proposed independently by Ho *et al.*³⁵ to combine the Gutzwiller approach with the DFT. The spirits of our method and their proposal are almost the same; however, they differ in the definition of the interaction and double-counting terms. It remains to be justified which way should be the best in future.

V. RESULTS AND DISCUSSIONS FOR REALISTIC SYSTEMS

The above proposed LDA+G method was implemented in our Beijing Simulation Tool for Atom Technology (BSTATE) code,³⁶ which uses plane-wave ultrasoft pseudopotential method, with projected Wannier function for the definition of local orbitals. We have applied the method to study several typical systems, where the strong e-e interactions play important roles. They are nonmagnetic metal SrVO₃, magnetic metals Fe and Ni, AF insulator NiO, and unconventional superconductor Na_{1-x}CoO₂. Some of the results have been published^{15,29} with emphasis on particular issues in each example. On the other hand, the main purpose of this full paper is to present the whole formalism of LDA+G and to demonstrate its advantage, namely, what knowledge can be gained beyond LDA or LDA+ U . Therefore, to keep the

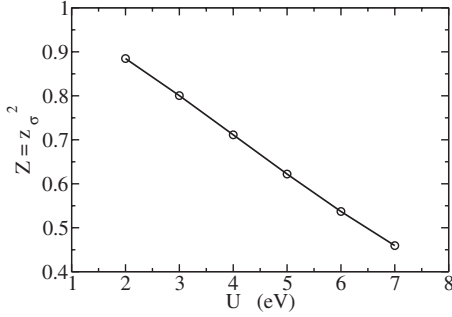


FIG. 6. The calculated Z factor as function of U for SrVO_3 using LDA+G method.

completeness of our present paper, here we would like to concentrate on the physical consequence of our method by grouping all results together. We will discuss all those results in a totally different manner, such that we can understand the LDA+G method better.

A. Band narrowing and mass renormalization

An essential quantity included in the LDA+G method is the kinetic renormalization factor $Z = z_\sigma^2$ due to the dynamic correlation. The z_σ factors are orbital dependent, and can be self-consistently obtained from the energy minimization. Under the Gutzwiller approximation, the Z factor can be also understood as the quasiparticle weight. It has been widely recognized that LDA-type calculations overestimate the bandwidth of correlated electron systems. The error bar could be as large as an order (such as in heavy-fermion system) depending on the strength of correlation. We will show here that this band-narrowing (or mass-renormalization) physics can be correctly obtained from the LDA+G method. For example, SrVO_3 is an intermediately correlated metal with $3d-t_{2g}^1$ configuration. It has simple cubic perovskite crystal structure, and magnetic instabilities are not involved in the ground-state property.^{33,37} Although the LDA calculation can correctly predict the nonmagnetic metallic nature of the ground state, the calculated bandwidth is about 40% wider than photoemission observation,³⁸ and the estimated effective mass is about two to three times lower than experimental results from specific heat and susceptibility. On the other hand, all these features can be improved by LDA+G calculations, and correct band narrowing and mass renormalization can be obtained as shown in Figs. 6 and 7 by using reasonable U (~ 5.0 eV). To gain further understanding, here we would also like to compare the results to that obtained by LDA+ U method. In the LDA+ U , only the interaction energy part is corrected over LDA, and the kinetic part is not renormalized, as already discussed in Sec. IV. Therefore, LDA+ U cannot explain the observed large renormalization as shown in Fig. 7, where the density of states (DOS) obtained by LDA+ U almost coincides with that by LDA. Finally, we will also show below that the band narrowing and mass renormalization are such important quantities and common advantage of LDA+G that it is encountered for all the examples we studied.

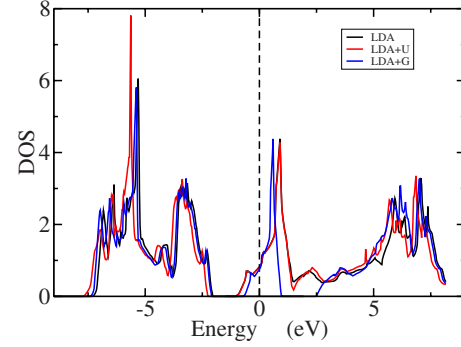


FIG. 7. (Color online) The calculated density of states for SrVO_3 using LDA, LDA+ U , and LDA+G methods. We used the $U=5.0$ eV and $J=1.0$ eV, and the electron DOS (rather than quasiparticle DOS) is shown, in the calculations of LDA+G.

B. Improved spin polarization

Except for the band renormalization, we will show here that the spin polarization of magnetic systems can be also improved to certain extent. To understand the physics better, we would like to divide the mechanisms of spin polarization into two parts: (1) The intersite exchange (or the spatial long-range exchange); and (2) the intrasite exchange (mostly the interorbital Hund coupling). Such a separation is not rigorous, but is just for the physical understanding. It is important to note that in our formalism, the spatial intersite part remains to be treated by LDA level, and only the intrasite part is improved explicitly. Of course, through the charge-density self-consistency, the intersite part may be also tuned slightly, but it is not a main effect. It is therefore understood that the issues related to the intersite exchange, such as the spin spatial fluctuation or the geometrically frustrated spin systems, cannot be improved through the LDA+G treatment.

Even if for the intrasite interaction, it is treated both in LDA+ U and in LDA+G, what will be the difference? In the LDA+ U , it is treated from the static mean-field level, which always tends to give larger spin polarization than that in LDA for positive effective $U_{\text{eff}} (=U-J)$. On the other hand in the LDA+G method, the dynamic effects are included and the intrasite (interorbital) charge and spin fluctuations are all included in a better way. It is in this sense that the results by LDA+G should be more reasonable. To demonstrate the effect of LDA+G on spin polarization, here we would like to show three examples:

(1) For ferromagnetic (FM) bcc Fe, as shown in Figs. 8 and 9, the calculated magnetic moment in LDA+ U is always larger than that in LDA, and is significantly overestimated compared to experiments. On the other hand, in LDA+G, this overestimation by LDA+ U is suppressed.

(2) For the bulk fcc Ni, the calculated moment by LDA+G is even smaller than that in LDA, in better agreement with experiments (see Table I).

(3) For $\text{Na}_{1-x}\text{CoO}_2$, the LDA level calculations predict that the system is magnetic for all the doping range; the LDA+ U calculations even enhance the tendency to be magnetic, in contrast to experimental observation. However, using LDA+G, we show in Ref. 29 that the ground state is actually nonmagnetic for the intermediate doping range

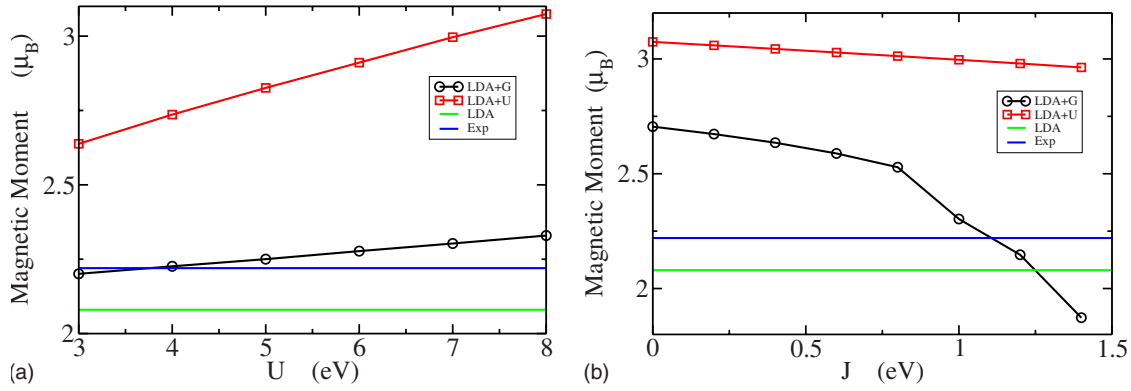


FIG. 8. (Color online) The calculated magnetic moment (per Fe) of bcc FM Fe as function of U and J , by using different methods.

(around $0.3 < x < 0.5$), in nice agreement with experiments.

C. Total energy and equilibrium properties

A big advantage of LDA-type calculations based on DFT is its ability to get the ground-state total energy accurately. Here we will show that, by explicitly treating the interaction term through our LDA+G formalism, the calculated total energy and equilibrium properties of correlated electron systems can be also improved significantly. Bulk Fe and Ni are typical magnetic metals with intermediate correlations, where LDA produces big error bar for the ground-state properties in comparison to experiments. For Fe, the LDA even fails to predict the correct bcc FM ground state (although GGA correctly does so, the reason is not clearly understood). The results, summarized in Table I, show that most of the discrepancies are systematically improved, compared with experiments, suggesting the advantages of present scheme. First of all, the bcc FM ground state is now correctly predicted by LDA+G (see Ref. 15 for original figure). We therefore understand that the failure of LDA to predict the correct ground state is due to its underestimation of strong on-site correlation. Second, the calculated equilibrium volume, bulk modulus, magnetic moment, specific-heat coefficient, and bandwidth are all improved in a systematic way by a simple fixed interaction strength ($U=7.0$ eV and $J=1.0$ eV). This is in sharp contrast to that obtained in LDA+ U ; for instance, the LDA+ U may also get the correct equilibrium volume by certain U value, but the obtained magnetic moment will be unreasonably larger than experimental results if the same U is used.

D. Large gap AF ordered insulator

Now we come to discussions for the large gap AF ordered insulator with integer occupation, where LDA+ U works well. We will show that the LDA+G actually gives similar results in this limit. The reason is very straightforward as has been pointed out in the formalism. In the present LDA+G scheme, both the on-site level and the kinetic energy should be renormalized due to the presence of interaction term. However, in the case that long-range ordering is established with integer occupation, if the energy gap is big, each orbital should be close to either fully occupied or totally empty,

because the charge fluctuation between the states should be small. In this limit, the kinetic renormalization Z factor will be very close to unity, and Ψ_G returns back to Ψ_0 . Therefore, the kinetic renormalization is very small, and only the renormalization to the on-site level takes effect; this is exactly just the limit that is obtained in LDA+ U . As we have shown in the calculations for NiO,¹⁵ the obtained electronic structure is very similar to that of LDA+ U . However please note that even for the AF long-range ordered insulators, if the band gap is small and the spin moment is far away from integer, the dynamic processes crossing the band gap may also take effect. In this case, the Z factor will be no longer unity, and of course, the results by LDA+G will be different from that of LDA+ U , and the one by LDA+G should be closer to reality. We expect that this situation may happen in the LaTiO₃,⁴⁰ where the gap is about 0.2 eV and the calculated moment from LDA+ U is much larger than that observed experimentally.

E. Effect of charge-density self-consistency

Here we will show that the charge-density self-consistency is really important for the calculations on realistic systems, and we take Na_{1-x}CoO₂, a typical multiorbital system, as an example. As we have pointed out in our recent

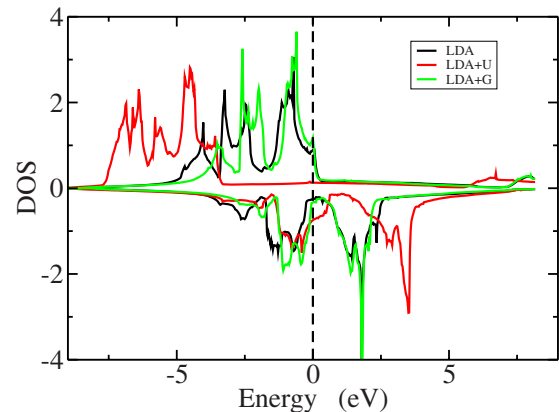


FIG. 9. (Color online) The calculated DOSs of bcc FM Fe using different methods. The parameters $U=7.0$ eV and $J=1.0$ eV are used in these calculations.

TABLE I. The calculated property parameters for bcc FM Fe and fcc FM Ni in comparison with experimental results. They are equilibrium lattice constant a_0 , bulk modulus B , spin magnetic moment M , specific-heat coefficient γ , and the occupied energy bandwidth W . The experimental data are from Ref. 39. (This table is a reproduction of our results that were published in Ref. 15.)

		a_0 (Bohr)	B (GPa)	M (μ_B)	γ ($\frac{\text{mJ}}{\text{K}^2 \text{mol}}$)	W (eV)
Fe	LDA	5.21	227	2.08	2.25	3.6
	LDA+G	5.39	160	2.30	3.52	3.2
	Expt.	5.42	168	2.22	3.1, 3.69	3.3
Ni	LDA	6.49	250	0.59	4.53	4.5
	LDA+G	6.61	188	0.50	6.9	3.2
	Expt.	6.65	186	0.42, 0.61	7.02	3.2

paper,²⁹ all the issues discussed above, such as the band narrowing, spin polarizations, and orbital fluctuations, are encountered in $\text{Na}_{1-x}\text{CoO}_2$, and systematic improvements are obtained through LDA+G treatment. However, we want to take $\text{Na}_{1-x}\text{CoO}_2$ as an example to demonstrate the importance of charge self-consistency because several post-LDA techniques (without charge self-consistency) have been applied to this compound and conflicting results are obtained.^{28,41} The issue is related to the relative splitting of energy level between e'_g and a_{1g} states, and the appearance of e'_g hole pockets at the Fermi surface (for $x=0.3$). If the splitting is large, the e'_g orbital will be totally occupied, and there will be no e'_g hole pockets at the Fermi surface. Starting from different Hamiltonians fitted to LDA band structure, advanced techniques such as Gutzwiller or DMFT have been applied in post-LDA scheme. However, one of the results suggests the absence of e'_g hole pockets,²⁸ and the other suggests the appearance.⁴¹ It is now understood⁴² that the main reason is due to the difference in the fitted tight-binding Hamiltonian; namely, the crystal-field splittings (or the on-site energies) in the two studies are different. In our LDA+G method, full charge self-consistency is achieved and no tight-binding fitting is required. Only after such kind treatment, the discrepancy can be nicely resolved.²⁹ On the other hand, because of the feedback effect in the charge self-consistency, the on-site level renormalization which is overestimated by post-LDA techniques is now suppressed as shown in Fig. 10.

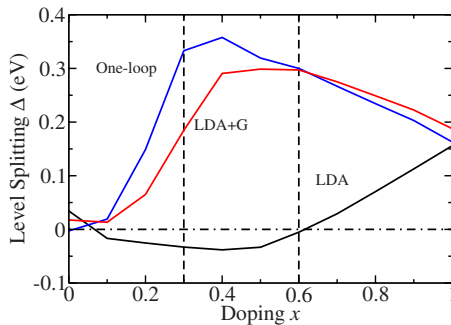


FIG. 10. (Color online) The calculated level splitting between the a_{1g} and the e'_g states for $\text{Na}_{1-x}\text{CoO}_2$. The original figure is obtained from Ref. 29. The one-loop result corresponds to the calculation without charge-density self-consistency.

In summary, we have shown in this full paper the detailed formalism of LDA+Gutzwiller method and its firm derivation from the GDFT. By comparing the results to that obtained by DMFT, we have shown that the energy resolution of Gutzwiller approach is pretty good for the ground-state determination. It is computationally cheaper, and yet with dynamic fluctuations included. The calculated results for several typical systems demonstrate that it can be widely applied to many of the correlated electron systems with quality beyond LDA+ U .

ACKNOWLEDGMENTS

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APPENDIX

In this appendix, we will prove several equations discussed in the text part. We will pay special attention to when and how GA is applied. Even when a variational ansatz is given for a lattice model, evaluation of expectation value is not straightforward. GA is a systemic approximation to make the evaluation accessible. The spirit of GA actually is to neglect Wick contractions between operators with different site or orbital indices. Thus in the following we often need to Fourier transform the expression into real space and then apply GA.

1. Proof of Eq. (8)

First we note that by choosing $\lambda_{i\Gamma} = \sqrt{\frac{m_{i\Gamma}}{m_{i\Gamma}^0}}$, $|\Psi_G\rangle$ is normalized under GA, $\langle \Psi_G | \Psi_G \rangle = \prod_i \langle \Psi_0 | \hat{P}_i^2 | \Psi_0 \rangle = \prod_i \sum_{\Gamma} \frac{m_{i\Gamma}}{m_{i\Gamma}^0} \langle \Psi_0 | \hat{m}_{i\Gamma} | \Psi_0 \rangle = \prod_i (\sum_{\Gamma} m_{i\Gamma}) = 1$. In the first equality we separate the average of a projection operator string into the product of single site averages.

Then the expectation value of kinetic energy is

$$\begin{aligned}
\langle \Psi_G | H_0 | \Psi_G \rangle &= \sum_{i,j} t_{ij}^{\sigma\sigma'} \langle \Psi_0 | \hat{P}_i C_{i\sigma}^\dagger \hat{P}_i \hat{P}_j C_{j\sigma'} \hat{P}_j | \Psi_0 \rangle \\
&\times \langle \Psi_0 | \prod_{i' \neq i,j} \hat{P}_{i'}^2 | \Psi_0 \rangle \\
&= \sum_{i,j} \sum_{\Gamma_i, \Gamma_i'} t_{ij}^{\sigma\sigma'} \sqrt{\frac{m_{\Gamma_i} m_{\Gamma_i'} m_{\Gamma_j} m_{\Gamma_j'}}{m_{\Gamma_i}^0 m_{\Gamma_i}^0 m_{\Gamma_j}^0 m_{\Gamma_j}^0}} \\
&\quad \Gamma_j, \Gamma_j' \\
&\times \langle \Psi_0 | \hat{m}_{i,\Gamma_i'} C_{i\sigma}^\dagger \hat{m}_{i,\Gamma_i} \hat{m}_{j,\Gamma_j} C_{j\sigma'} \hat{m}_{j,\Gamma_j'} | \Psi_0 \rangle,
\end{aligned}$$

contractions from site $i' \neq i, j$ and sites i, j . To evaluate the expectation value we define

$$\hat{m}_{i,\Gamma_i'} = \hat{l}_{i,\Gamma_i} \hat{n}_{i\sigma},$$

$$\hat{m}_{i,\Gamma_i} = \hat{l}_{i,\Gamma_i} (1 - \hat{n}_{i\sigma}),$$

$$\hat{m}_{j,\Gamma_j'} = \hat{l}_{j,\Gamma_j} \hat{n}_{j\sigma'},$$

$$\hat{m}_{j,\Gamma_j} = \hat{l}_{j,\Gamma_j} (1 - \hat{n}_{j\sigma'}),$$

where in the first equality we adopt GA to neglect all Wick

where \hat{l}_{i,Γ_i} (\hat{l}_{j,Γ_j}) are projection operators for orbital other than σ (σ'). Then we have

$$\begin{aligned}
\langle \Psi_0 | \hat{P} H_0 \hat{P} | \Psi_0 \rangle &= \sum_{i,j} \sum_{\Gamma_i, \Gamma_i'} t_{ij}^{\sigma\sigma'} \sqrt{\frac{m_{\Gamma_i} m_{\Gamma_i'} m_{\Gamma_j} m_{\Gamma_j'}}{m_{\Gamma_i}^0 m_{\Gamma_i}^0 m_{\Gamma_j}^0 m_{\Gamma_j}^0}} \langle \Psi_0 | \hat{l}_{i,\Gamma_i} \hat{l}_{i,\Gamma_i'} \hat{l}_{j,\Gamma_j} \hat{l}_{j,\Gamma_j'} | \Psi_0 \rangle \\
&\quad \Gamma_j, \Gamma_j' \\
&\quad \langle \Psi_0 | \hat{n}_{i\sigma} C_{i\sigma}^\dagger (1 - \hat{n}_{i\sigma}) (1 - \hat{n}_{j\sigma'}) C_{j\sigma'} \hat{n}_{j\sigma'} | \Psi_0 \rangle D_{\Gamma_i \Gamma_i'}^\sigma D_{\Gamma_j \Gamma_j'}^{\sigma'*} \\
&= \sum_{i,j} \sum_{\Gamma_i, \Gamma_i' \Gamma_j, \Gamma_j'} t_{ij}^{\sigma\sigma'} \frac{\sqrt{m_{\Gamma_i} m_{\Gamma_i'} D_{\Gamma_i \Gamma_i'}^\sigma}}{\sqrt{n_{i\sigma}^0 (1 - n_{i\sigma}^0)}} \frac{\sqrt{m_{\Gamma_j} m_{\Gamma_j'} D_{\Gamma_j \Gamma_j'}^{\sigma'*}}}{\sqrt{n_{j\sigma'}^0 (1 - n_{j\sigma'}^0)}} \langle \Psi_0 | C_{i\sigma}^\dagger C_{j\sigma'} | \Psi_0 \rangle = \sum_{i,j,\sigma} z_{i\sigma} z_{j\sigma'} t_{ij}^{\sigma\sigma'} \langle \Psi_0 | C_{i\sigma}^\dagger C_{j\sigma'} | \Psi_0 \rangle. \quad (\text{A1})
\end{aligned}$$

The expectation value of interaction part is

$$\langle \Psi_G | H_{\text{int}} | \Psi_G \rangle = \sum_i \sum_\Gamma E_\Gamma \frac{m_{i,\Gamma}}{m_{i,\Gamma}^0} \langle \Psi_0 | \hat{m}_{i,\Gamma} | \Psi_0 \rangle = \sum_i \sum_\Gamma E_\Gamma m_{i,\Gamma}. \quad (\text{A2})$$

Putting Eqs. (A1) and (A2) together, we will have Eq. (8) shown in Sec. II.

2. Proof of $\gamma_{k\sigma} = z_\sigma$

In this section, we prove that $\gamma_{k\sigma} = z_\sigma$ under GA; here we focus on quasiparticle sector without loss of generality. To compute $\langle \Phi_{k\sigma}^p | C_{k\sigma}^\dagger | G \rangle$, we first Fourier transform the operators into real space then apply GA,

$$\begin{aligned}
\langle \Phi_{k\sigma}^p | C_{k\sigma}^\dagger | \Psi_G \rangle &= \frac{1}{N} \sum_{I,J} e^{ik(I-J)} \langle \Psi_0 | C_{J\sigma} \hat{P} C_{I\sigma}^\dagger \hat{P} | \Psi_0 \rangle \\
&= \frac{1}{N} \sum_I \langle \Psi_0 | C_{I\sigma} \hat{P} C_{I\sigma}^\dagger \hat{P} | \Psi_0 \rangle + \frac{1}{N} \sum_{I \neq J} e^{ik(I-J)} \langle \Psi_0 | C_{J\sigma} \hat{P} C_{I\sigma}^\dagger \hat{P} | \Psi_0 \rangle \\
&= \frac{z_\sigma}{N} \sum_I \langle \Psi_0 | C_{I\sigma} C_{I\sigma}^\dagger | \Psi_0 \rangle + \frac{z_\sigma}{N} \sum_{I \neq J} e^{ik(I-J)} \langle \Psi_0 | C_{J\sigma} C_{I\sigma}^\dagger | \Psi_0 \rangle \\
&= z_\sigma \langle \Psi_0 | C_{k\sigma} C_{k\sigma}^\dagger | \Psi_0 \rangle = z_\sigma \theta(\varepsilon_{k\sigma} - \mu_F).
\end{aligned}$$

Similarly, we could prove that under GA $\langle \Phi_{k\sigma}^h | C_{k\sigma} | \Psi_G \rangle = z_\sigma \langle \Psi_0 | C_{k\sigma}^\dagger C_{k\sigma} | \Psi_0 \rangle = z_\sigma \theta(\mu_F - \varepsilon_{k\sigma})$. Thus we have $\gamma_{k\sigma} = z_\sigma$ under GA. Also note that under GA the k dependence of the Z is missing; only the fact that whether $\varepsilon_{k\sigma}$ is above or below the Fermi surface matters.

3. Evaluation of $E_{k\sigma}^p$

First we show that the quasiparticle state is normalized under GA:

$$\begin{aligned}\langle \Phi_{k\sigma}^p | \Phi_{k\sigma}^p \rangle &= \frac{1}{N} \sum_I \sum_{\Gamma} \frac{m_{\Gamma}}{m_{\Gamma}^0} \langle \Psi_0 | C_{I\sigma} \hat{m}_{I;\Gamma} C_{I\sigma}^{\dagger} | \Psi_0 \rangle + \frac{1}{N} \sum_{I \neq J} e^{ik(I-J)} \sum_{\Gamma_I, \Gamma_J} \frac{m_{\Gamma_I} m_{\Gamma_J}}{m_{\Gamma_I}^0 m_{\Gamma_J}^0} \langle \Psi_0 | C_{J\sigma} \hat{m}_{J;\Gamma_J} \hat{m}_{I;\Gamma_I} C_{I\sigma}^{\dagger} | \Psi_0 \rangle \\ &= \frac{1}{N} \sum_I \langle \Psi_0 | C_{I\sigma} C_{I\sigma}^{\dagger} | \Psi_0 \rangle + \frac{1}{N} \sum_{I \neq J} e^{ik(I-J)} \langle \Psi_0 | C_{J\sigma} C_{I\sigma}^{\dagger} | \Psi_0 \rangle = \langle \Psi_0 | C_{k\sigma} C_{k\sigma}^{\dagger} | \Psi_0 \rangle = 1 \quad \text{for } \epsilon_{k\sigma} > \mu_F.\end{aligned}$$

Then the kinetic energy for spin σ species reads

$$\begin{aligned}\langle \Phi_{k\sigma}^p | \sum_{i,j} t_{ij} C_{i\sigma}^{\dagger} C_{j\sigma} | \Phi_{k\sigma}^p \rangle &= \frac{1}{N} \sum_{I,J} e^{ik(I-J)} \sum_{i,j} t_{ij} \langle \Psi_0 | C_{J\sigma} \hat{P} C_{i\sigma}^{\dagger} C_{j\sigma} \hat{P} C_{I\sigma}^{\dagger} | \Psi_0 \rangle \\ &= \sum_{i,j} t_{ij} \langle \Psi_0 | C_{I\sigma} \hat{P} C_{i\sigma}^{\dagger} C_{j\sigma} \hat{P} C_{I\sigma}^{\dagger} | \Psi_0 \rangle + \sum_{J \neq I} e^{ik(I-J)} \sum_{i,j} t_{ij} \langle \Psi_0 | C_{J\sigma} \hat{P} C_{i\sigma}^{\dagger} C_{j\sigma} \hat{P} C_{I\sigma}^{\dagger} | \Psi_0 \rangle.\end{aligned}$$

For the first term since $i \neq j$, there is a constraint that $I \neq i$ and $I \neq j$; otherwise the expression vanishes. Then it becomes equal to

$$\sum_{i,j} t_{ij} \langle \Psi_0 | C_{I\sigma} \hat{P}_I \hat{P}_i \hat{P}_j C_{i\sigma}^{\dagger} C_{j\sigma} \hat{P}_i \hat{P}_j \hat{P}_I C_{I\sigma}^{\dagger} | \Psi_0 \rangle = \left(\sum_{\Gamma_I \supset \sigma} \frac{m_{\Gamma_I}}{n_{\sigma}^0} \right) z_{\sigma}^2 \sum_{i,j} t_{ij} \langle \Psi_0 | C_{I\sigma} C_{i\sigma}^{\dagger} C_{j\sigma} C_{I\sigma}^{\dagger} | \Psi_0 \rangle = z_{\sigma}^2 \sum_{i,j} t_{ij} \langle \Psi_0 | C_{I\sigma} C_{i\sigma}^{\dagger} C_{j\sigma} C_{I\sigma}^{\dagger} | \Psi_0 \rangle.$$

For the second term, we have four cases: $I=j$ but $J \neq i$; $I \neq j$ but $J=i$; $I=j, J=i$; and $I \neq j, J \neq i$. Following previous technique, one could find out that for each of the cases the projection operator \hat{P} gives a z_{σ}^2 factor. Thus,

$$\langle \Phi_{k\sigma}^p | \sum_{i,j} t_{ij} C_{i\sigma}^{\dagger} C_{j\sigma} | \Phi_{k\sigma}^p \rangle = z_{\sigma}^2 \sum_{i,j} t_{ij} \langle \Psi_0 | C_{k\sigma} C_{i\sigma}^{\dagger} C_{j\sigma} C_{k\sigma}^{\dagger} | \Psi_0 \rangle = z_{\sigma}^2 \sum_k \epsilon_{k\sigma} \langle \Psi_0 | C_{k\sigma}^{\dagger} C_{k\sigma} | \Psi_0 \rangle + z_{\sigma}^2 \epsilon_{k\sigma},$$

while the kinetic energy for $\mu \neq \sigma$ is:

$$\begin{aligned}\langle \Phi_{k\sigma}^p | \sum_{i,j,\mu} t_{ij} C_{i\mu}^{\dagger} C_{j\mu} | \Phi_{k\sigma}^p \rangle &= \sum_J e^{ik(I-J)} \sum_{i,j,\mu} t_{ij} \langle \Psi_0 | C_{J\sigma} \hat{P} C_{i\mu}^{\dagger} C_{j\mu} \hat{P} C_{I\sigma}^{\dagger} | \Psi_0 \rangle \\ &= \left[\langle \Psi_0 | C_{I\sigma} C_{I\sigma}^{\dagger} | \Psi_0 \rangle + \sum_{J \neq I} e^{ik(I-J)} \langle \Psi_0 | C_{J\sigma} C_{I\sigma}^{\dagger} | \Psi_0 \rangle \right] z_{\mu}^2 \sum_{i,j} t_{ij} \langle \Psi_0 | C_{i\mu}^{\dagger} C_{j\mu} | \Psi_0 \rangle \\ &= \sum_{k\mu} z_{\mu}^2 \epsilon_{k\mu} \langle \Psi_0 | C_{k\mu}^{\dagger} C_{k\mu} | \Psi_0 \rangle.\end{aligned}$$

Following the same routine, one could prove that

$$\langle \Phi_{k\sigma}^p | H_I | \Phi_{k\sigma}^p \rangle = N \sum_{\Gamma} E_{\Gamma} m_{\Gamma} + O(1).$$

Putting the kinetic and interaction energies together, we get $\langle \Phi_{k\sigma}^p | H | \Phi_{k\sigma}^p \rangle = \sum_{k\mu} z_{\mu}^2 \epsilon_{k\mu} \langle 0 | C_{k\mu}^{\dagger} C_{k\mu} | 0 \rangle + N E_{\Gamma} m_{\Gamma} + z_{\sigma}^2 \epsilon_{k\sigma} + O(1)$.

Putting the constant into chemical potential, we have

$$E_{k\sigma}^p = \frac{\langle \Phi_{k\sigma}^p | H | \Phi_{k\sigma}^p \rangle}{\langle \Phi_{k\sigma}^p | \Phi_{k\sigma}^p \rangle} - E_G = z_{\sigma}^2 (\epsilon_{k\sigma} - \mu_F).$$

For quasihole state, one could get similar results.

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