LDA + Gutzwiller method for correlated electron systems

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Abstract – We develop an \textit{ab initio} density functional theory incorporating with Gutzwiller variational approach, which is equally applicable to the ground state of systems ranging from weakly correlated metals to strongly correlated insulators with long-range ordering. We have applied this theory to calculate the electronic structures of three different systems: non-magnetic metal SrVO$_3$, ferromagnetic metals Fe and Ni, and antiferromagnetic insulator NiO. Ground-state properties are all obtained in good agreement with experiments within the same approach.

Despite the great successes of local density approximation (LDA) and generalized gradient approximation (GGA) for simple metals and band insulators, the applications of density functional theory (DFT) are limited for correlated electron systems, a class of important systems in condensed-matter physics. It has long been a challenge to develop an \textit{ab initio} method, which has the accuracy and parameter-free character of DFT and can be equally applied to all kinds of systems. Along this line, there have been a lot of efforts [1–3] in recent years to explicitly take into account the effect of strong on-site electron interaction, which is treated insufficiently in LDA or GGA. The LDA + U method [1] adopted the orbital-dependent Hartree-like scheme, which has been successfully applied to predict the insulating feature of strongly correlated systems with long-range ordering. However, it fails for intermediated correlated metallic systems. In more recently developed dynamic mean-field theory combined with LDA (LDA + DMFT) [3], one uses the same effective Hamiltonian, but treats the interaction by the proper calculation of frequency-dependent electron self-energy. The method is quite successful [3], but the calculation of the frequency-dependence makes the method less practical. It is therefore important to develop a unified approach which is practical and applicable to both the correlated metals and the strongly correlated insulators.

We will present in this paper that the difficulty can be overcome through the proper combination of DFT with Gutzwiller variational approach [4], which is commonly used in model studies for the strongly correlated systems [5–7]. As a result, the LDA + Gutzwiller method is proposed. Our study is motivated by the previous work, which applied the Gutzwiller method onto an effective Hamiltonian extracted from LDA [8–10]. We show here that a fully self-consistent LDA + Gutzwiller method can be developed, and it is practical to be implemented in the existing computation scheme. We have used this newly developed method to calculate three typical systems: the non-magnetic metal SrVO$_3$, ferromagnetic metals Fe, Ni, and antiferromagnetic insulator NiO. The results are in good agreement with experiments, and demonstrate significant improvement over LDA and LDA + U. A unified approach to describe various of ground-state properties is thus constructed.

The basic idea of DFT and the Kohn-Sham equation is to find a reference system (usually non-interacting system with single Slater determinant wave function $|\Psi_0\rangle$), which has the same charge density as the true system but the kinetic energy can be explicitly computed. In such a way, all unknown parts are moved into the exchange-correlation energy $E_{xc}$. Unfortunately, the exact functional form of $E_{xc}$ is not known, and the LDA for $E_{xc}$ is not sufficient for materials containing the partial filled narrow bands, such as 3$d$ or 4$f$ states. To improve this, the idea of the LDA + U or the LDA + DMFT method is to correct
the LDA Hamiltonian $H^{LDA}$ by including explicitly e-e interaction of local orbitals and remove the double-counting part from the LDA. Therefore in both LDA + U and LDA + DMFT, the Hamiltonian reads

$$H^{LDA+U} = H^{LDA} + \sum_{i\alpha\beta} U_{\alpha\beta} n_{i\alpha} n_{i\beta} - H_{dc},$$  \hspace{1cm} (1)

where $|i\alpha\rangle$ is a set of local spin-orbitals with occupation number $n_{i\alpha}$ for lattice site $i$, and $U_{\alpha\beta}$ gives the interaction strength between the orbitals, $H_{dc}$ is the double-counting term as treated in LDA + U [1].

Now the problem to be solved is to minimize the total energy through the variational principle. In the Kohn-Sham formulation of the LDA + U method, this is done with respect to the single Slatterd determinant trial wave function $|\Psi_0\rangle$, which can improve the interaction part of the total energy and leave the non-interacting kinetic part unchanged. In LDA + DMFT, however, both the single-particle wave functions and the spectral density of the local orbitals are considered to be the variational parameters. The enlargement of the variational space makes the LDA + DMFT work quite well for both interaction and kinetic part of the total energy. But the price of LDA + DMFT is that we have to deal with the frequency dependence of the self-energy for each local orbitals, which makes it very expensive.

An alternative way for the problem is to improve the trial wave functions of the reference system, which gives the same charge density as true system (as required by DFT) but the kinetic part can be improved as well. This is what we will do in the following. It is known that $|\Psi_0\rangle$ is not good, and a better candidate for the trial wave function is the Gutzwiller wave function [4], which is basically the lattice version of the Jastrow-type wave function for quantum liquid and has been extensively used in the strongly correlated systems [5]. It is defined as

$$|\Psi^G\rangle = \hat{P}|\Psi_0\rangle,$$  \hspace{1cm} (2)

$$\hat{P} = \prod_{\Gamma} [1 + (\lambda_{\Gamma} - 1)|i, \Gamma\rangle \langle i, \Gamma|].$$  \hspace{1cm} (3)

The projection operator $\hat{P}$ is used to reduce the weight of configurations for the local orbitals with relatively high energy. Here $\Gamma$ denotes the $\Gamma$-th many-body configuration for the local orbitals in given unit cell $i$ and $\lambda_{\Gamma}$ are the variational parameters describing the weight for given configuration $\Gamma$. Therefore our task is to minimize the total energy with respect to the Gutzwiller wave function:

$$E^{LDA+G}(\rho) = \langle \Psi^G | H^{LDA} | \Psi^G \rangle - E_{dc} + \langle \Psi^G | H_{\text{loc}} | \Psi^G \rangle, \hspace{1cm} (4)$$

Thanks to the recent progresses for Gutzwiller approach, although the exact solution of the above expectation is unknown, the Gutzwiller approximation (GA) is a very tractable approximation for the multiband Hubbard model and has been proven to be exact in the limit of infinite dimensions. In the present paper, we apply the GA directly to the LDA Hamiltonian rather than the tight-binding form extracted from it. To do so, we only need a set of local orbitals $|\alpha\rangle$ where we implement the local correlation effect. Following reference [8], we can derive the total energy under GA as

$$E^{LDA+G}(\rho) \approx \langle \Psi_0 | H^{LDA+G} | \Psi_0 \rangle - E_{dc} + \sum_{i,\Gamma} E_{1 \Gamma}^m m_t^{\Gamma},$$  \hspace{1cm} (5)

with the Gutzwiller effective Hamtonian in momentum $(k)$ space given as

$$H^{LDA+G}_k = [\hat{Q} + (1 - \hat{R})] H^{LDA}[\hat{Q} + (1 - \hat{R})] + \sum_{\alpha k} (1 - Z_\alpha^2) \epsilon_0^\alpha |\alpha k\rangle \langle \alpha k|,$$  \hspace{1cm} (6)

$$\hat{Q} = \sum_{\alpha k} Z_\alpha |\alpha k\rangle \langle \alpha k|, \hspace{1cm} \hat{R} = \sum_{\alpha k} |\alpha k\rangle \langle \alpha k|,$$  \hspace{1cm} (7)

where $E_{\Gamma}$ is the eigenvalue and $m_t^{\Gamma}$ is the weight of the $\Gamma$-th configuration, $\epsilon_0^\alpha$ is the on-site energy of each local orbital. The key quantities here are $Z_\alpha$ $(0 < Z_\alpha < 1)$, which describe the kinetic energy renormalization of local orbitals, and can be expressed in terms of $m_t$ through

$$Z_\alpha = \sum_{\Gamma} \langle \Gamma | C^\dagger_{\alpha \Gamma} C_{\alpha \Gamma} | \Gamma \rangle \frac{m^\Gamma m_r^\Gamma}{\sqrt{n_\alpha (1 - n_\alpha)}}.$$  \hspace{1cm} (8)

The main strategy of the above formalism is that, kinetic energy of correlated orbitals are renormalized by factor $Z_\alpha$, while all other non-correlated orbitals are taken into account by the projector $(1 - \hat{R})$. Therefore under GA, the total energy can be expressed again as the functional of a non-interacting wave function $\Psi_0$, but with additional variational parameters of the weighting factors $m_r$, along with the following necessary constraint:

$$\sum_{\Gamma} \langle \Gamma | C^\dagger_{\alpha \Gamma} C_{\alpha \Gamma} | \Gamma \rangle m_r^\Gamma = n_\alpha = \sum_k \langle \Psi_0 | C^\dagger_{\alpha k} C_{\alpha k} | \Psi_0 \rangle.$$  \hspace{1cm} (9)

The original Gutzwiller variational parameters $\lambda_{\Gamma}$ can be obtained by $\lambda_{\Gamma} = m_r^{\Gamma}/m_t^{\Gamma}$, with $m_t^{\Gamma} = \langle \Psi_0 | \Gamma \rangle$.

Having the above equations, it is easy to obtain Kohn-Sham–like equations by the variational approach,

$$\frac{\partial E^{LDA+G}(\rho)}{\partial \Psi_0} = 0, \hspace{1cm} \frac{\partial E^{LDA+G}(\rho)}{\partial m_r^\Gamma} = 0.$$  \hspace{1cm} (10)

The charge density under GA can be constructed as

$$\rho^{LDA+G}(r) = \langle \Psi_0 | \hat{Q} + (1 - \hat{R}) | r \rangle |\Psi_0 \rangle$$

$$+ \sum_{\alpha k} (1 - Z_\alpha^2) \langle \Psi_0 | \alpha k \rangle \langle \alpha k | \Psi_0 \rangle \rho_{\alpha k}(r).$$ \hspace{1cm} (11)

In practice, two steps are followed. 1) For fixed $m_r$, the $|\Psi_0\rangle$ is optimized by solving the effective Kohn-Sham-like
equations. This step is basically the same as for all other LDA calculations. 2) For fixed |\Psi_0\>, mγ are optimized by solving a set of saddle point equations [11], whose dimension is the total number of configurations Γ (for instance 210 for five d-orbitals). The second step is an addition to the LDA calculations, however, with the numerical technique we proposed in our previous paper [11], the computational cost is rather small. For instance, the minimization for five d-orbitals can be done within 30 seconds on a PC. The final solution of the system is obtained until the charge density (and total energy) is self-consistently converged.

The above-proposed LDA + Gutzwiller method was implemented in our BSTATE (Beijing Simulation Tool for Atom Technology) code [12], which uses the plane-wave ultra-soft pseudo-potential method. For the local basis, the physical choice is the Wannier function constructed from the atomic orbital. This was done by using the projected Wannier function method [13] in our calculations. For the interaction term, only on-site density-density interactions are considered in the present studies. Several typical systems were calculated, and the results are discussed below.

1. Non-magnetic correlated metal: SrVO3

SrVO3 is a correlated metal with 3d-t\textsubscript{2g} configuration. The simple cubic perovskite crystal structure and non-magnetic electronic state make it an ideal test material [14]. The one-particle spectrum calculated with LDA is poorly compared with experiments [15]. The main problems are: 1) the calculated band width is about 40% wider than photoemission observation; 2) the estimated effective mass is about 2–3 times lower than experimental results from specific heat and susceptibility; 3) the photoemission peak observed around 2 eV below Fermi level (E\textsubscript{F}) is not understood.

However, most of these features can be understood from our LDA + Gutzwiller calculations. We choose the 3d Wannier function as the interacting local orbits with effective interaction energy U = 5.0 eV following the literatures [14]. Figure 1 shows the calculated band structure and the density of states of quasi-particle spectrum. It is clear that the band width is reduced by about 40% compared with LDA. From the calculated quasi-particle spectrum it is straightforward to calculate the effective mass enhancement (m*\gamma/m), which is 2.1 times larger than LDA result. All these results are in good consistency with experiments [15], and much better than that obtained from LDA. Finally, it is worth to make the comment: since all the quasi particle part has been well treated in the present scheme (the incoherent part is not included yet), and no DOS is found around the −2 eV region, it further suggests that the observed photoemission peak in this region should be incoherent as suggested by other studies [14].

2. Magnetic correlated metals: Fe and Ni

Bulk Fe and Ni are typical magnetic metals with intermediate correlations. For Fe, the LDA fails to predict the bcc FM ground state, although GGA correctly does so. Both LDA and GGA overestimate the band width by about 10–20% compared with experiments [16]. For Ni, the problems are more serious, the band width is overestimated by about 30%, and the spin polarization is hardly compared with experiments [9]. For such intermediate correlated metals, the LDA + U method may improve one or two discrepancies to some extent, while the price to be paid is that other predicted properties become even worse than LDA.

To be realistic, we first determine the effective U from constrained-LDA calculations [17] to be 7.0 eV (Fe) and 9.0 eV (Ni) for the choice of our local orbital, and Hund’s coupling J is fixed to be 1.0 eV (a common choice for 3d elemental metal). The results, summarized in table 1, figs. 2 and 3, show that most of the discrepancies are systematically corrected compared with experiments, suggesting the advantages of present scheme. In particular, the following improvements are significant: 1) The band width renormalization is correctly predicted and effective mass enhancement (specific-heat coefficient) can be well compared with experiments. 2) The calculated lattice parameter, bulk modulus and magnetic moment show systematic improvement. Finally, we want to point out that for the down-spin band of Ni, around the X-point near E\textsubscript{F}, one of the bands predicted by LDA to be above E\textsubscript{F}, is now correctly predicted to be below E\textsubscript{F}, in agreement with recent AREPS data [9].

3. AF correlated insulator: NiO

In the present LDA + Gutzwiller scheme, both effective on-site level renormalization and kinetic renormalization are included, while only the former is considered in the LDA + U scheme. For the intermediately correlated metallic systems, the kinetic energy renormalization is significant and this is the reason why the LDA + U scheme fails. However, for the strongly correlated insulator with long-range ordering (large U limit), where the effective on-site level renormalization dominates, the LDA + U
Table 1: 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 $\gamma$, and the occupied energy band width $W$. The experimental data are from ref. [18].

|       | $a_0$ (bohrs) | $B$ (GPa) | $M$ ($\mu_B$) | $\gamma$ (mJ mol$^{-1}$K$^{-2}$) | $W$ (eV) |
|-------|---------------|-----------|----------------|--------------------------------|-----------|
| Fe    | LDA           | 5.21      | 227            | 2.08                           | 2.25      | 3.6       |
|       | LDA + G       | 5.39      | 160            | 2.30                           | 3.52      | 3.2       |
|       | Exp.          | 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       |
|       | Exp.          | 6.65      | 186            | 0.42, 0.61                     | 7.02      | 3.2       |

Fig. 2: The calculated total energy as a function of volume for different phases of bulk Fe by the LDA + Gutzwiller method. The bcc FM ground state is correctly predicted.

Fig. 3: The calculated band structure of fcc FM Ni.

scheme works well. Following our formalism, if $Z_\alpha$ goes to 1, $|\Psi_G\rangle$ is reduced to $|\Psi_0\rangle$, then the LDA + U results should be recovered. As an example, we calculated the correlated insulator NiO. We apply the method to the ground state with long-range AF ordering, rather than the paramagnetic insulating phase at high temperature. Our results show that the kinetic energy renormalization factor $Z_\alpha$ is close to unity (0.98 in average), because the occupation number of local orbitals is very close to 1 or 0 in this AF ordered phase. The obtained electronic structure is similar to that of LDA + U (the obtained magnetic moment and band gap are 1.7 $\mu_B$ and 2.5 eV in LDA + U, and 1.6 $\mu_B$ and 2.2 eV in LDA + G, using $U = 7.0$ eV and $J = 1.0$ eV). However, for some of the AF insulators, the band gap is small and the moment is far away from integer, we expect that the kinetic energy renormalization will also contribute (i.e. $Z_\alpha$ is away from 1).

Finally, we should comment on the choices of the interaction $U$ and the double-counting term which are difficult points also for LDA + U and LDA + DMFT approaches. 1) There is no unified way to determine the U yet, nevertheless if the s, p hybridizations are switched off in our calculations, a smaller $U$ can produce the same size of renormalization ($Z_\alpha$). Similar results are also obtained by Weber et al. [19]. 2) The conventional double-counting term (like that used in LDA + U or LDA + DMFT) [1] is used at the present stage, however it remains to be justified whether this is the best choice.

In summary, we have shown that the Gutzwiller approach can be well combined with the DFT through the variational principle. As a result, a fully self-consistent LDA + Gutzwiller method (which allows for total energy calculations) is developed, and it can be equally applied to weakly and strongly correlated systems (for the ground-state ordered phase). The orbital fluctuation (which is missing in LDA + U) is included and the method is practical. As long as low-energy physics is concerned, both the spectral weight ($Z$-factor) and the dispersion relation of the quasi-particles can be obtained, and can be well compared with ARPES results.

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