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Gutzwiller density functional theory for correlated electron systems

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We develop a density functional theory (DFT) and formalism for correlated electron systems by taking as reference an interacting electron system that has a ground state wave function which exactly obeys the Gutzwiller approximation for all one-particle operators. The solution of the many-electron problem is mapped onto the self-consistent solution of a set of single-particle Schrödinger equations, analogously to standard DFT-local density approximation calculations.

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Over the last several decades, first-principles total energy calculations using density functional theory based on the local density approximation (LDA) or generalized gradient approximation (GGA) have been well developed into a theoretical tool with strong predictive capability for a large number of materials.[1–4] However, there are important classes of materials involving strongly correlated electrons, ranging from high-T_c superconducting compounds and various other transition metal oxide materials to f-electron-element bearing materials, where the current LDA and GGA approaches fail in fundamental ways. There have been intensive studies on new approaches to remedy the situation, such as LDA+U,[5] LDA dynamical mean field theory,[6–9] self-interaction correction local spin density,[10] and hybrid functionals.[11,12] Although these approaches partially address the issues related to strongly correlated electron systems, a comprehensive and generally accepted predictive theory with the quality of the LDA for normal metals, alloys, and compounds is still lacking for materials containing strongly correlated electrons. To address this problem, we propose in this paper a density functional theory that goes beyond the LDA through a self-consistent solution of the many-body ground state using the Gutzwiller approximation[13] for interacting electron systems within a first-principles framework.

The Hohenberg-Kohn theorem states that the ground state energy of an electron system is a functional of the electron density.[1] Kohn and Sham[2] took this a step further by expressing the energy of a real system in terms of the energy of a fictitious system of noninteracting electrons that has the same density as the real system. This led to a system of noninteracting electrons moving in an effective potential that can be solved through the iterative solution of a set of one-electron Schrödinger equations within the LDA for the exchange-correlation energy. The current first-principles density functional calculations are based on this set of effective one-electron Kohn-Sham equations. It should be noted that the Hohenberg-Kohn density functional theorem is true for any electron system, including strongly correlated electron systems. The failure of the Kohn-Sham approach for strongly correlated electron systems, in our view, is largely due to the choice of noninteracting electron as the reference system. By carefully choosing a reference system which includes the most essential strong correlations, yet still can be cast into a set of one-electron Schrödinger equations through variational principles, a density functional formalism for treating strongly correlated electron systems can be derived and implemented following the spirit of Kohn and Sham.[2]

In the approach we propose here, instead of defining the kinetic energy functional to be the kinetic energy of a noninteracting electron gas with the same density, we will define the kinetic energy functional to have a simple analytical form corresponding to the frequently used Gutzwiller approximation for a system of electrons with on-site-only correlations.[13–18] The expectation of any one-particle operator (e.g., the electron kinetic energy and the electron density) under the Gutzwiller approximation can be expressed in terms of a noninteracting one-particle density matrix with renormalized weight due to adjustments from strong correlation effects.[13–18] We will show that. within the Gutzwiller approximation, the interacting many-electron problem can be mapped onto a noninteracting system with an effective potential. The exact Coulomb interactions can be included for a predetermined set of localized configurations while the local density approximation is used for all the remaining exchange-correlation contributions.

The choice of including electron correlations using the Gutzwiller approximation is motivated by previous work where it has been shown to interpolate well between the two regimes of strong electron correlation (large-U limit) and small electron correlation (small-U limit). Another importance of the Gutzwiller approach is the correct description of highly correlated states near the Fermi level. The LDA can be viewed as an extension of Hartree-Fock theory to density functional theory; we view our present scheme as an extension of quantum chemical coupled-cluster calculations to density functional theory. In our scheme, the variational parameters are the single-particle electron wave functions for the localized and delocalized electrons and the occupancy of the various localized configurations at each atom in the unit cell. Like the LDA, the formulation is from first principles with all Coulomb and exchange interactions determined self-consistently. There are no adjustable parameters.

According to the Hohenberg-Kohn density functional theorem, the ground state energy of a multielectron system is a functional of the electron density ρ

$$\langle\Psi|\hat{H}|\Psi\rangle = E[\rho]. \tag{1}$$

Instead of taking as reference a noninteracting electron gas with the same density as the exact many-electron system, the density functional in our present theory is determined by taking as reference an *interacting* electron system:

$$\langle\Psi|\hat{H}|\Psi\rangle = \langle\Psi_G|\hat{T}+\hat{V}_{\text{ion}}|\Psi_G\rangle + E_{\text{xc}}[\rho] + \frac{1}{2}\int \rho(\mathbf{r})v(\mathbf{r},\mathbf{r}')\rho(\mathbf{r}')d^3rd^3r'. \quad (2)$$

The reference system is chosen to have the same electron density $\rho(\mathbf{r})$ as the ground state of the exact multielectron system and to have a ground state wave function $|\Psi_G\rangle$ that obeys exactly the Gutzwiller approximation for all one-particle operators,

$$\hat{O} = \sum_{m=1}^{N} \hat{O}_m. \quad (3)$$

In the Gutzwiller approximation, for each one-particle operator acting on $|\Psi_G\rangle$, we can define a corresponding renormalized operator $\hat{O}_G$, acting on the underlying Hartree-like wave function $|\Psi_0\rangle$ used in generating $|\Psi_G\rangle$ in the Gutzwiller approach such that

$$\langle\Psi_G|\hat{O}|\Psi_G\rangle = \langle\Psi_0|\hat{O}_G|\Psi_0\rangle, \quad (4)$$

where

$$\langle\phi_{i\alpha}|\hat{O}_G|\phi_{j\beta}\rangle = z_{i\alpha}O_{i\alpha,j\beta}z_{j\beta} \quad (5)$$

if $(i,\alpha)\neq(j,\beta)$, while

$$\langle\phi_{i\alpha}|\hat{O}_G|\phi_{i\alpha}\rangle = O_{i\alpha,i\alpha}. \quad (6)$$

Therefore we have

$$\langle\Psi_G|\hat{O}|\Psi_G\rangle = {\sum_{i\alpha,j\beta}}' z_{i\alpha}z_{j\beta}O_{i\alpha,j\beta}\langle\Psi_0|c^\dagger_{i\alpha}c_{j\beta}|\Psi_0\rangle + \sum_{i\alpha} O_{i\alpha,i\alpha}\langle\Psi_0|c^\dagger_{i\alpha}c_{i\alpha}|\Psi_0\rangle, \quad (7)$$

where $\{\phi_{i\alpha}\}$ is a local orbital basis for the system, a subset L of which represents localized electrons in the system, and $\Sigma'_{i\alpha,j\beta}$ indicates summation with the self-term $(i,\alpha)=(j,\beta)$ omitted. $|\Psi_0\rangle$ is the uncorrelated Hartree-like wave function corresponding to $|\Psi_G\rangle$. The z factors are renormalization weights for the localized part of the one-particle density matrix,

$$z_{i\alpha} = \frac{\sum_{\Gamma_i,\Gamma_i'}\sqrt{p^{\alpha}_{\Gamma_i,\Gamma_i'}}}{\sqrt{n_{i\alpha}(1-n_{i\alpha})}} \quad (8)$$

where $p^{\alpha}_{\Gamma,\Gamma'}=p_{i,\Gamma}p_{i,\Gamma'}|\langle\Gamma'|c_{i\alpha}|\Gamma\rangle|^2$ is the probability for a transition between two atomic configurations Γ_i and Γ_i' that results in the increase of the occupation of the single-particle state α at site i by 1. The summation is over all configurations on site i.[16,18] For nonlocalized orbitals $z_{i\alpha}=1$. In our present notation, α includes both the orbital and spin indices and

$$n_{i\alpha} = \langle\Psi_0|c^\dagger_{i\alpha}c_{i\alpha}|\Psi_0\rangle. \quad (9)$$

The $z_{i\alpha}$ are therefore functions of the orbital occupation $\{n_{i\alpha}\}$ and the probabilities $p^{\alpha}_{\Gamma,\Gamma'}$. The $p^{\alpha}_{\Gamma,\Gamma'}$ can be expressed in terms of the probabilities $p_i(\Gamma)$ for a local configuration Γ.[16,18] The set of local orbitals in L and the set of local configurations $\{\Gamma_i\}$ with nonzero probabilities are specified for the system.

Under the Gutzwiller approximation, the electron density is defined as

$$\rho(\mathbf{r}) = {\sum_{i\alpha,j\beta}}' z_{i\alpha}z_{j\beta}\phi^*_{i\alpha}(\mathbf{r})\phi_{j\beta}(\mathbf{r})\langle\Psi_0|c^\dagger_{i\alpha}c_{j\beta}|\Psi_0\rangle + \sum_{i\alpha}|\phi_{i\alpha}(\mathbf{r})|^2\langle\Psi_0|c^\dagger_{i\alpha}c_{i\alpha}|\Psi_0\rangle. \quad (10)$$

We can also define the localized electron density $\rho_l(\mathbf{r})$ by a similar expression, except that the summation is restricted to α and β in L.

We will choose $E_{\text{xc}}[\rho]$ to be of the form

$$E_{\text{xc}}[\rho] = \sum_{i\Gamma} p_i(\Gamma)U_\Gamma + \int d^3r(\rho-\rho_l)\varepsilon_{\text{xc}}(\rho) - \frac{1}{2}\int\int \rho_l(\mathbf{r})v(\mathbf{r},\mathbf{r}')\rho_l(\mathbf{r}')d^3rd^3r'. \quad (11)$$

We require our system to be the same as the regular LDA system in the limit when there are no localized electrons. This can be achieved if we choose $\varepsilon_{\text{xc}}(\rho)$ to be the same as in the LDA. In the limit when all electrons are localized our system becomes a multiband Hubbard Hamiltonian. U_Γ is a sum of Slater integrals representing the Coulomb repulsion between localized orbitals on the same site in the configuration Γ.

The variational degrees of freedom in our system are $\{p_i(\Gamma)\}$ and $|\Psi_0\rangle$. Since $|\Psi_0\rangle$ can be expressed as a simple product of one-particle wave functions $\{\psi_{n\mathbf{k}}\}$, it follows that

$$\langle\Psi_0|c^\dagger_{i\alpha}c_{j\beta}|\Psi_0\rangle = \sum_{n,\mathbf{k}} f_{n,\mathbf{k}}\langle\psi_{n\mathbf{k}}|\phi_{i\alpha}\rangle\langle\phi_{j\beta}|\psi_{n\mathbf{k}}\rangle, \quad (12)$$

where $n,\mathbf{k}$ are the usual band indices and $f_{n,\mathbf{k}}$ is 1 for occupied states and 0 for empty states. The variational parameters in our calculations are $\{p_i(\Gamma)\}$ and $\{\psi_{n\mathbf{k}}\}$ with the constraints that $\{\psi_{n\mathbf{k}}\}$ are normalized to 1.

A set of single-electron equations can be derived using the variational principle by taking the derivatives of the energy functional Eq. (2) with respect to $\{\psi_{n\mathbf{k}}\}$ and $\{p_i(\Gamma)\}$, keeping in mind that the density $\rho(\mathbf{r})$, the localized density $\rho_l(\mathbf{r})$, the exchange-correlation functional $\varepsilon_{\text{xc}}(\rho)$, and the parameters $z_{i\alpha}$ are defined above. This set of equations can be solved self-consistently to give the band structures and total energies of the correlated electron system.

By taking the derivatives with respect to $\{\psi_{n\mathbf{k}}\}$ we have

$$\hat{H}_{\text{eff}}\psi_{n\mathbf{k}} = \lambda_{n\mathbf{k}}\psi_{n\mathbf{k}} \quad (13)$$

with effective Hamiltonian

$$\hat{H}_{\text{eff}} = \hat{H}^l_G + \sum_{i\alpha\beta} 2e_{i\beta}\frac{\partial \ln z_{i\beta}}{\partial n_{i\alpha}}\hat{P}_{i\alpha}, \quad (14)$$

where the first term $\hat{H}^l_G$ is the Gutzwiller-renormalized operator of $\hat{H}^l$ and

$$\hat{H}^l = \hat{T} + \hat{V}_{\text{ion}} + \hat{V}_H + \mu_{\text{xc}} - \hat{P}_l(\hat{V}_H^l + \varepsilon_{\text{xc}})\hat{P}_l \tag{15}$$

is the effective mean-field potential with the localized-localized electron interaction contributions subtracted out. $\hat{V}_H$ and $\hat{V}_H^l$ are the mean-field Coulomb potential (Hartree potential) due to the total and localized charge, respectively,

$$\mu_{\text{xc}} = \frac{\partial(\rho - \rho_l)\varepsilon_{\text{xc}}(\rho)}{\partial\rho}, \tag{16}$$

while $\hat{P}_l$ is the projection operator on the localized subspace L, i.e., $\hat{P}_l\phi_{i\alpha}=\phi_{i\alpha}$ for $\alpha \in L$ (localized electron orbitals) and $\hat{P}_l\phi_{i\alpha}=0$ otherwise.

The second term in Eq. (14) adds back the localized-localized electron contribution to the effective potential (subtracted from the first term) according to the Gutzwiller approximation. In the second term, $\hat{P}_{i\alpha}$ is the projection operator on $\phi_{i\alpha}$ and

$$e_{i\alpha} = \frac{1}{2}\sum_{n\mathbf{k}} f_{n\mathbf{k}}\langle\psi_{n\mathbf{k}}|\hat{P}_{i\alpha}\hat{H}_G^l + \hat{H}_G^l\hat{P}_{i\alpha}|\psi_{n\mathbf{k}}\rangle - \hat{H}^l_{i\alpha,i\alpha}n_{i\alpha}. \tag{17}$$

The derivatives over the local configuration probabilities $\{p_i(\Gamma)\}$ yield

$$0 = U_\Gamma + 2\sum_{i\alpha} e_{i\alpha}\frac{\partial \ln z_{i\alpha}}{\partial p_i(\Gamma)}. \tag{18}$$

This is a set of self-consistency criteria to be satisfied by $\{p_i(\Gamma)\}$.

The set of equations in (13) and (18) can be solved iteratively to obtain a self-consistent solution for $\{p_i(\Gamma)\}$ and $\{\psi_{n\mathbf{k}}\}$ and the total energy of the system evaluated according to Eqs. (1)–(12).

The specific derivation of our density functional approach is based on the Gutzwiller method. It is, however, possible to formally generalize the approach and set up a density functional for an arbitrary solvable interacting many-electron reference system, independent of the specific aspects of the Gutzwiller formalism. To put it in a more general context, we discuss these aspects of our approach. A crucial ingredient of the density functional formulation by Kohn and Sham is to choose the kinetic energy functional $T[\rho]$ to be the kinetic energy of a system of independent electrons in a potential $\hat{V}_s$ that yields the ground state density $\rho(\mathbf{r})$. Our approach differs from this key starting point by Kohn and Sham by defining $T[\rho]$ as the kinetic energy of a system of *interacting* electrons. We then assume that one can again formulate an effective many-body problem with Hamiltonian

$$\hat{H}_s = \hat{T} + \hat{V}_s + \hat{U}_s \tag{19}$$

that yields the ground state density $\rho(\mathbf{r})$ through an appropriate choice of the single-particle potential $\hat{V}_s$. $\hat{U}_s$ still contains explicit interactions among the electrons. We then use the wave function $|\Psi_s\rangle$ of this correlated reference system to define the kinetic energy functional

$$T[\rho] = \langle\Psi_s|\hat{T}|\Psi_s\rangle. \tag{20}$$

This necessitates a modified functional for $E_{\text{xc}}[\rho]$ which is no longer the only term where correlation effects enter. A self-consistent set of density functional equations emerges for any choice of $|\Psi_s\rangle$ that allows for an evaluation of the functional derivative $\delta T[\rho]/\delta\rho(\mathbf{r})$. The Gutzwiller wave function $|\Psi_s\rangle=|\Psi_G\rangle$ discussed above, and other Jastrow-type wave functions, are examples. The close formal connection to a noninteracting electron system [see Eq. (4)] makes the analysis of the kinetic energy feasible and leads to the mapping of the many-particle problem onto a set of effective single-particle Schrödinger equations.

We can make further progress in our analysis of $E_{\text{xc}}[\rho]$ by using the coupling constant integration approach of Ref. 19. We first make a specific choice $\hat{U}_s=\hat{P}\hat{U}\hat{P}$ for the interaction term, where $\hat{P}$ projects onto the configuration space of the strongly interacting electrons, e.g., the local $3d$, $4f$, or $5f$ electrons. We then introduce the Hamiltonian

$$\hat{H}_\lambda = \hat{T} + \hat{U}_s + \lambda(\hat{U} - \hat{U}_s) + \hat{V}(\lambda) \tag{21}$$

with varying coupling constant λ, where the potential $\hat{V}(\lambda)$ equals the nuclear potential $\hat{V}_0$ for $\lambda=1$ and is assumed to yield a density $\rho(\mathbf{r})$ independent of λ for $\lambda < 1$. With the help of the Hellmann-Feynman theorem, we obtain an explicit expression for the exchange-correlation functional

$$E_{\text{xc}}[\rho] = \langle\Psi_s|\hat{U}_s|\Psi_s\rangle + \int d^3r[\rho\varepsilon_{\text{xc}}(\mathbf{r}) - \rho_l\varepsilon_{\text{xc},l}(\mathbf{r})] - \frac{1}{2}\int\int \rho_l(\mathbf{r})v(\mathbf{r},\mathbf{r}')\rho_l(\mathbf{r}')d^3r\, d^3r' \tag{22}$$

that is independent of the specifics of the above Gutzwiller approach. The exchange correlation potential $\varepsilon_{\text{xc},l}(\rho)$ of the localized orbitals is found to be

$$\varepsilon_{\text{xc},l}(\mathbf{r}) = \frac{1}{2}\int d^3r'\rho_l(\mathbf{r}')v(\mathbf{r},\mathbf{r}')[g_l(\mathbf{r},\mathbf{r}') - 1], \tag{23}$$

where $g_l(\mathbf{r},\mathbf{r}')=\int_0^1 d\lambda\Sigma_{\sigma\sigma'}\langle\hat{P}b^\dagger_{\sigma\sigma'}(\mathbf{r},\mathbf{r})b_{\sigma\sigma'}(\mathbf{r},\mathbf{r})\hat{P}\rangle_\lambda/\rho_l(\mathbf{r})\rho_l(\mathbf{r}')$ is the two-particle correlation function of localized states with $b_{\sigma\sigma'}(\mathbf{r},\mathbf{r})=\psi_{\sigma'}(\mathbf{r}')\psi_\sigma(\mathbf{r})$. Comparing this result with Eq. (11), we identify $\Sigma_{i\Gamma}p_i(\Gamma)U_\Gamma=\langle\Psi_s|\hat{U}_s|\Psi_s\rangle$ and find that we made the approximate choice $\varepsilon_{\text{xc},l}(\rho)\simeq\varepsilon_{\text{xc}}(\rho)$. Then, the second term in Eq. (22) becomes simply $\int d^3r(\rho-\rho_l)\varepsilon_{\text{xc}}(\rho)$. This simple choice reproduces correctly the limit of the ordinary density functional theory of Kohn and Sham in the case without localized orbitals. A similar form was also shown to be very successful in describing the nonlinear exchange-correlation interactions between core and valence charge densities.[20]

An important physical consequence of our approach is its ability to combine two, seemingly distinct, mechanisms for screening the Coulomb interaction between electrons. Usually, screening is understood as a response of the particle density in the vicinity of a charged object and many aspects of it are appropriately incorporated in the usual Kohn-Sham density functional formalism. On the other hand, in the case of strong electron-electron correlations, the Coulomb interaction can also be screened via a reorganization of the many-body state, for example in the form of strong band renormalizations, amounting to a drastic change in the kinetic energy of the electrons. These effects are at best poorly described in the usual density functional formalism. In our approach, through the self-consistent solution for $\{\psi_{n\mathbf{k}}\}$ and $\{p_i(\Gamma)\}$, the system can respond to the addition of extra terms in the Hamiltonian (both in the external potential as well as in U_Γ). The approach has the advantage of combining both aspects of screening in a self-consistent way without resorting to model parameters or model Hamiltonians. This opens an additional perspective for the first-principles description of strong electron correlations in complex materials.

Our above derivation closely parallels the approach in the original Kohn-Sham paper. A more rigorous formulation of the LDA in terms of a constrained search approach avoids issues of representability of the electronic density. We note that it is possible to parallel our theory following that formulation also (details will be provided in a future presentation) and that the Kohn-Sham equations are identical for both formulations. In the present formulation, the results are sensitive to the choice of the localized orbitals. This issue can be addressed (in future work) by generalizing the Gutzwiller approach.

In summary, we have developed a density functional theory incorporating strongly correlated electronic effects into the kinetic energy functional within the Gutzwiller approximation. We show that a set of single-particle equations can be obtained from functional derivatives of the energy with respect to the orbitals included in the noninteracting one-particle density matrix with renormalized kinetic and potential operators. This set of equations can be solved self-consistently in a way similar to regular LDA calculations. In our scheme, the variational parameters are the single-particle electron wave functions for the localized and delocalized electrons and the occupancy of the various localized configurations at each atom in the unit cell. Like the LDA, and unlike many other correlated electron calculations available, the formulation is derived from first principles with all Coulomb and exchange-correlation interactions determined self-consistently. There are no adjustable parameters. We believe developments along these lines will be fruitful in extending the successful applications of density functional calculations to systems with important electron correlations.

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