

Beyond LDA: the Gutzwiller approach

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Gutzwiller density functional theory

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- Motivation: LDA calculations using Kohn-Sham approach are highly effective, but fails for systems with strong electron correlations
- Kohn-Sham approach introduces *kinetic energy functional* by comparing with a *non-interacting electron system*
- We introduce new kinetic energy functional using a new reference *interacting* electron system obeying the *Gutzwiller approximation*
- Resulting new density functional yields *self-consistent* one-particle Schroedinger equations that can be solved analogous to LDA
- Our scheme includes additional variational degrees of freedom corresponding to *occupation of local electron configurations* → first principles parameter-free DFT theory

Other methods

- Dynamical mean field theory
- LDA + U
- LDA + Gutzwiller

- Involve parameters U etc which has to be adjusted or calculated from separate LDA calculations; not clear what is the proper value of these parameters

Background

To solve many-electron systems in quantum mechanics

$$H = \sum_i -\frac{\hbar^2}{2m} \nabla_i^2 + \sum_{il} \left(-\frac{e^2}{4\pi\epsilon_0} \frac{Z_l}{|\vec{r}_i - \vec{R}_l|} \right) + \frac{1}{2} \sum_{i \neq j} \left(\frac{e^2}{4\pi\epsilon_0} \frac{1}{|\vec{r}_i - \vec{r}_j|} \right)$$

Three main approaches:

- Hartree-Fock method and its derivatives (quantum chemistry)
- Density functional theory (computational physics)
- Model Hamiltonian approach (many body physics)

Kohn-Sham DFT within LDA

- Hohenberg-Kohn theorem: the ground state energy of an electron system is a functional of the electron density
- Kohn-Sham LDA (local density approx.) uses a non-interacting electron system as reference

$$\langle \Psi | \hat{H} | \Psi \rangle = \langle \Psi_0 | \hat{T} | \Psi_0 \rangle + \langle \Psi_0 | \hat{V} | \Psi_0 \rangle + \frac{1}{2} \iint \rho(\vec{r}) v(\vec{r}, \vec{r}') \rho(\vec{r}') d\vec{r} d\vec{r}'$$
$$+ E_{xc}[\rho(r)]$$

$$E_{xc}[\rho(r)] = \int \rho(\vec{r}) \varepsilon_{xc}(\rho(\vec{r})) d\vec{r}$$

note : $\langle \Psi | \hat{H} | \Psi \rangle = \langle \Psi | \hat{T} | \Psi \rangle + \langle \Psi | \hat{V} + \hat{U} | \Psi \rangle$

Kohn-Sham DFT

Hohenberg-Kohn theorem:

The ground state energy of a many-electron system is a functional of the electron density

$$E_0[\rho] = T_0[\rho] + V_H[\rho] + E_{xc}^0[\rho] + \int V_{ion}(\mathbf{r}) \rho(\mathbf{r}) d^3r$$

$$V_H[\rho] = \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \iint \frac{\rho(\mathbf{r}) \rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3r d^3r'$$

Kohn-Sham approach:

Kinetic energy functional is expressed as the sum of kinetic energy of fictitious non-interacting electrons which keeps the same density as the real system

$$T_0[\rho] = \sum_i -\frac{\hbar^2}{2m} \langle \psi_i | \nabla_i^2 | \psi_i \rangle$$

$$\rho(\mathbf{r}) = \sum_i |\psi_i(\mathbf{r})|^2$$

Key to new approach

- Instead of just getting a better exchange-correlation functional, work on getting a better kinetic energy functional by using a better reference system

New density functional

$$\langle \Psi | \hat{H} | \Psi \rangle = \langle \Psi_G | \hat{T} + \hat{V}_{ion} | \Psi_G \rangle + \frac{1}{2} \iint \rho(\vec{r}) v(\vec{r}, \vec{r}') \rho(\vec{r}') d\vec{r} d\vec{r}' + E_{xc}[\rho(r)]$$

- Designate a subset \mathbf{l} of orbitals as representing localized electrons
- Replace non-interacting electron reference system with an interacting Gutzwiller $|\Psi_G\rangle = \hat{G}|\Psi_0\rangle$ \hat{G} projects out chosen local electronic configurations and suppress their amplitudes.
- Choice of Gutzwiller approach because
 1. Gutzwiller approach interpolates well between strong correlation and weak correlation regimes
 2. Analogy to coupled-cluster method in quantum chemistry: Expectation values can still be written in terms of one set of one particle wavefunctions

Gutzwiller approximation

exact in the limit of high orbital degeneracy

In the Gutzwiller approximation, the expectation of any one-particle operator acting on $|\Psi_G\rangle$, can be related to a corresponding renormalized operator acting on the underlying uncorrelated Hartree-like wavefunction $|\Psi_0\rangle$, such that

$$\langle \Psi_G | \hat{O} | \Psi_G \rangle = \sum'_{i,j,\alpha,\beta} z_{i\alpha} O_{i\alpha,j\beta} z_{j\beta} \langle \Psi_0 | c_{i\alpha}^\dagger c_{j\beta} | \Psi_0 \rangle + \sum_{i\alpha} O_{i\alpha,i\alpha} \langle \Psi_0 | c_{i\alpha}^\dagger c_{i\alpha} | \Psi_0 \rangle$$

$\{\phi_{i\alpha}\}$ is a local orbital basis for the system, a subset \mathbf{l} of which represents localized electrons in the system and Σ' indicates summation with the self term $i\alpha = j\beta$ omitted. $z = 1$ for orbitals not in \mathbf{l} , For localized orbitals in \mathbf{l} , z is a function of the probabilities of various local electron configurations at each site i .

$$z_{i\alpha} = \frac{1}{\sqrt{n_{i\alpha}^0 (1 - n_{i\alpha}^0)}} \sum_{H,H'} \sqrt{p_{iH} p_{iH'}} \left| \langle H | c_{i\alpha}^\dagger | H' \rangle \right|^2$$

New exchange-correlation functional

$$E_{xc}[\rho] = \sum_{i,\Gamma} U_{\Gamma} p_i(\Gamma) - \frac{1}{2} \iint \rho_{\ell} v \rho_{\ell} + \int (\rho \varepsilon_{xc}(\rho) - \rho_{\ell} \varepsilon_{xc}(\rho_{\ell}))$$

U_{Γ} is the Slater integral representing the Coulomb repulsion between localized orbitals on the same site in the configuration Γ . p is the probability of occurrence of the local configuration Γ at the site i .

We subtract off the mean field localized-localized electron Coulomb repulsion so that there is no double counting of the electron-electron interactions in our Hamiltonian.

For the delocalized electrons ($\rho - \rho_{\ell}$) we keep the Kohn-Sham treatment so our theory reduces to the Kohn-Sham theory when $\rho_{\ell} = 0$.

When all electrons are localized reduces to the multiband Hubbard hamiltonian

Beyond Hubbard and Gutzwiller

- Gutzwiller approximation applied strictly speaking to Hubbard hamiltonian with diagonal on-site term
- To go beyond this limitation, we divide orbitals into localized and delocalized part
- Solve on-site problem in localized subspace exactly
- Resulting hamiltonian can be mapped onto Hubbard hamiltonian ($U \rightarrow E$)
- Adopt Gutzwiller approx only for interactions between localized subspace and delocalized subspace

Choice of reference system

- Let $\hat{\psi}(\vec{r}) = \sum_{i,\alpha} \phi_{i\alpha}(\vec{r}) \hat{c}_{i\alpha}$ where $\{\phi_{i\alpha}\}$ is a mutually orthogonal local orbital basis for the system, a subset L of which represents localized orbitals at the various sites in the system.
- We choose our simplified interacting electron reference system to be represented by the following Hamiltonian:

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

Reference Hamiltonian

$$\widehat{H}_s = \widehat{T} + \widehat{V}_s + \widehat{U}_s$$

$$\widehat{T} = \sum_{i,j,\alpha,\beta} \langle \phi_{i\alpha} | \widehat{T} | \phi_{j\beta} \rangle c_{i\alpha}^\dagger c_{j\beta}$$

$$\widehat{V}_s = \sum_{i,j,\alpha,\beta} \langle \phi_{i\alpha} | \widehat{V}_s | \phi_{j\beta} \rangle c_{i\alpha}^\dagger c_{j\beta}$$

For \widehat{U}_s , we choose the projection of the two-particle Coulomb repulsion \widehat{U} onto the localized orbital subspace, including only on-site terms.

The remaining part of the two-body Coulomb repulsion term is assumed to be represented in a mean-field fashion in

$$\widehat{V}_s = V_{ion} + V_{scr}$$

Exact treatment for on-site Hamiltonian

- Treat on-site correlations between localized orbitals exactly by projecting H_s onto the localized subspace at each site.
- Exactly diagonalize the on-site Hamiltonian

$$\hat{H}_i = \sum_{\tilde{\Gamma}_i} E_i(\Gamma) |\Gamma_i\rangle \langle \Gamma_i|$$

- This includes all relevant on-site interactions: spin-orbit, crystal field, magnetic exchange, Hund's rule coupling etc.

Hamiltonian is now in Hubbard form

$$\widehat{H}_s = \sum_{\kappa, \kappa'} \mathcal{E}_{\kappa\kappa'} c_{\kappa}^{\dagger} c_{\kappa'} + \sum_{i, \alpha, \kappa} (w_{i\alpha, \kappa} c_{i\alpha}^{\dagger} c_{\kappa} + c.c.) + \sum_{i, \Gamma} E_i(\Gamma) b_{i, \Gamma}^{(l)\dagger} b_{i, \Gamma}^{(l)}$$

$$\mathcal{E}_{\kappa\kappa'} = \langle \phi_{\kappa} | \widehat{T} + \widehat{V}_s | \phi_{\kappa'} \rangle$$

$$w_{i\alpha, \kappa} = \langle \phi_{i\alpha} | \widehat{T} + \widehat{V}_s | \phi_{\kappa} \rangle$$

On-site interactions between localized states are treated exactly.

Interactions between localized and delocalized subspaces are mediated only by one-particle operators tractable by Gutzwiller approximation following Buenemann et al (1998, 2007)

Self-consistent solution of Hamiltonian

- Taking functional derivatives wrt the one particle wavefunctions in the underlying Hartree wavefunction, we can get a set of self-consistent one particle equations

analogous to Kohn-Sham theory.

$$\lambda_{n\vec{k}} \psi_{n\vec{k}} = \hat{H}_{eff} \psi_{n\vec{k}}$$

$$\hat{H}_{eff} = \hat{H}_G^\ell + \sum_{i,\alpha,\beta} 2e_{i\beta} \frac{\partial \ell n(z_{i\beta})}{\partial n_{i\alpha}} \hat{P}_{i\alpha}$$

the first term is the Gutzwiller-renormalized operator of the effective mean-field potential with the localized-localized electron-interaction contributions subtracted out

$$\hat{H}^\ell = \hat{T} + \hat{V}_{ion} + \hat{V}_H + \mu_{xc} - \hat{P}_\ell \left(\hat{V}_H^\ell + \mu_{xc}^\ell \right) \hat{P}_\ell$$

$\hat{P}_{i\alpha}$ are projection operators a specific localized orbital and \hat{P}_ℓ projects on the whole localized subspace \mathcal{L} .

The second term adds back the localized-localized electron contribution to the effective potential (subtracted from the first term) according to the Gutzwiller approximation

$$e_{i\alpha} = \frac{1}{2} \sum_{n,k} f_{nk} \left\langle \psi_{nk} \left| \hat{P}_{i\alpha} \hat{H}_G^\ell + \hat{H}_G^\ell \hat{P}_{i\alpha} \right| \psi_{nk} \right\rangle - H_{i\alpha,i\alpha}^\ell n_{i\alpha}$$

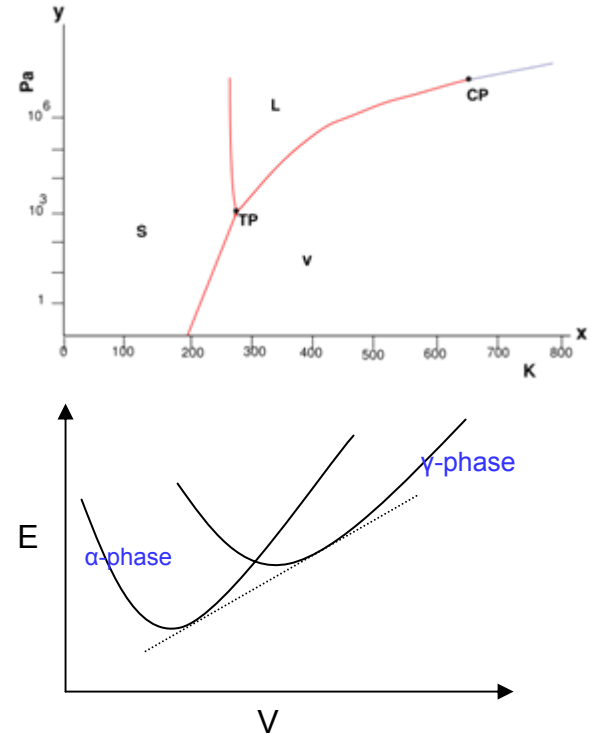
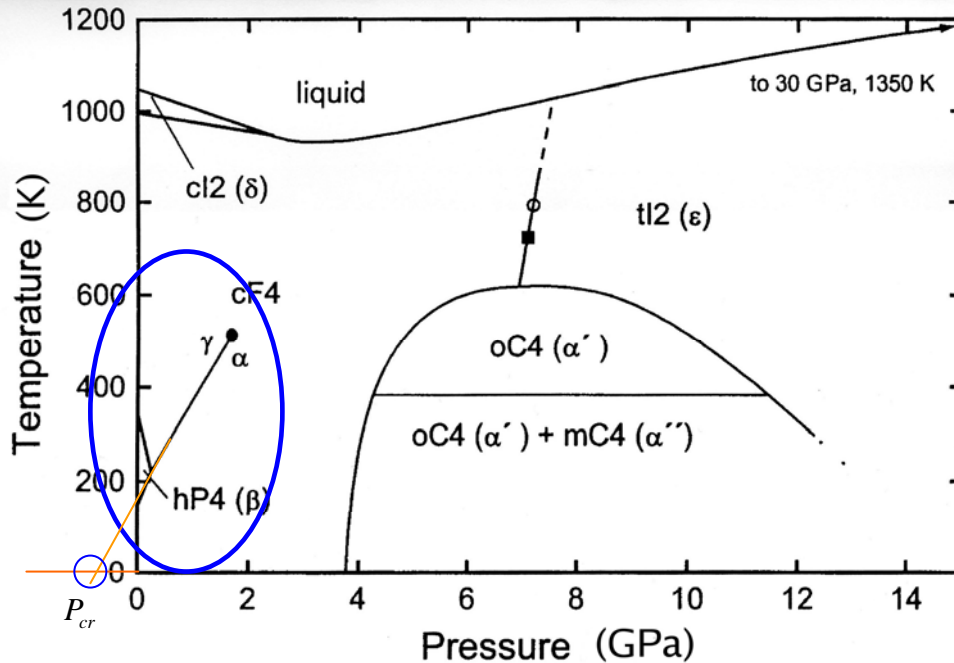
Additional variational degrees of freedom in the new theory: $p_i(\Gamma)$

- Derivatives wrt new degrees of freedom lead to auxiliary self-consistent criteria given by the set of equations:

$$0 = E_{\Gamma} + \sum_{\alpha} 2e_{i\alpha} \frac{\partial \ell n(z_{i\alpha})}{\partial p_i(\Gamma)}$$

This yields additional channels for screening the Coulomb repulsion from localized electrons via electronic correlations instead of the usual deformation of charge in usual LDA approach.

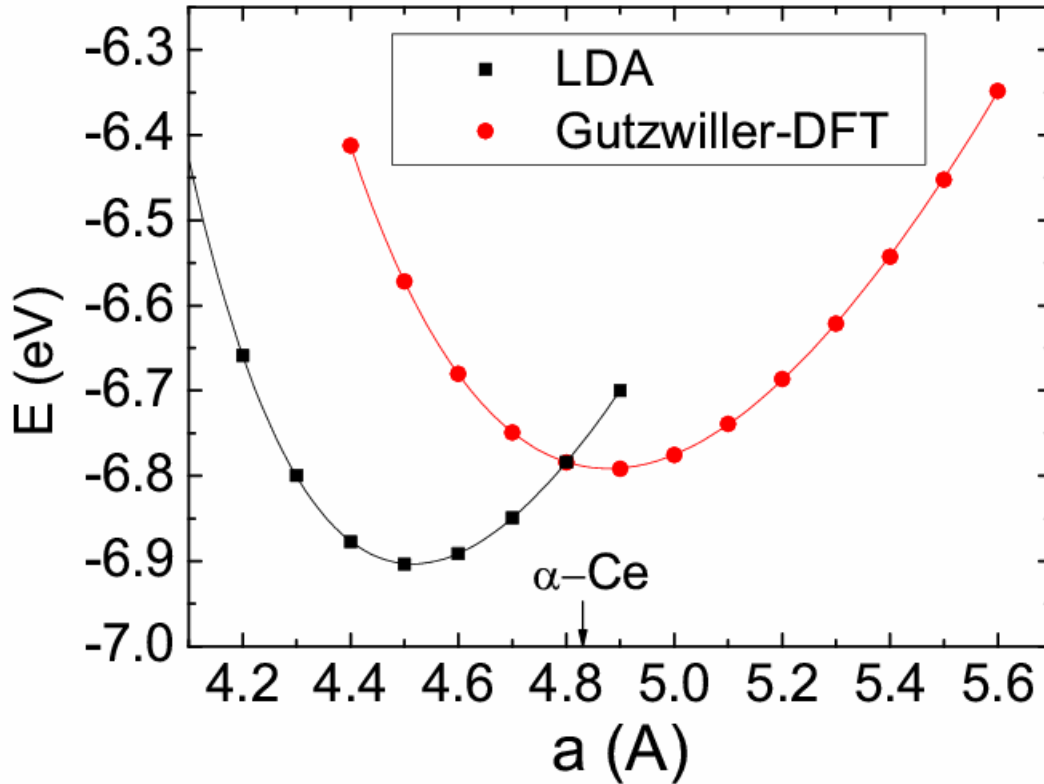
Application (Ce)



Ce exhibits an isostructural $\gamma \rightarrow \alpha$ phase transformation with a volume change of 17%.

Preliminary results: Ce

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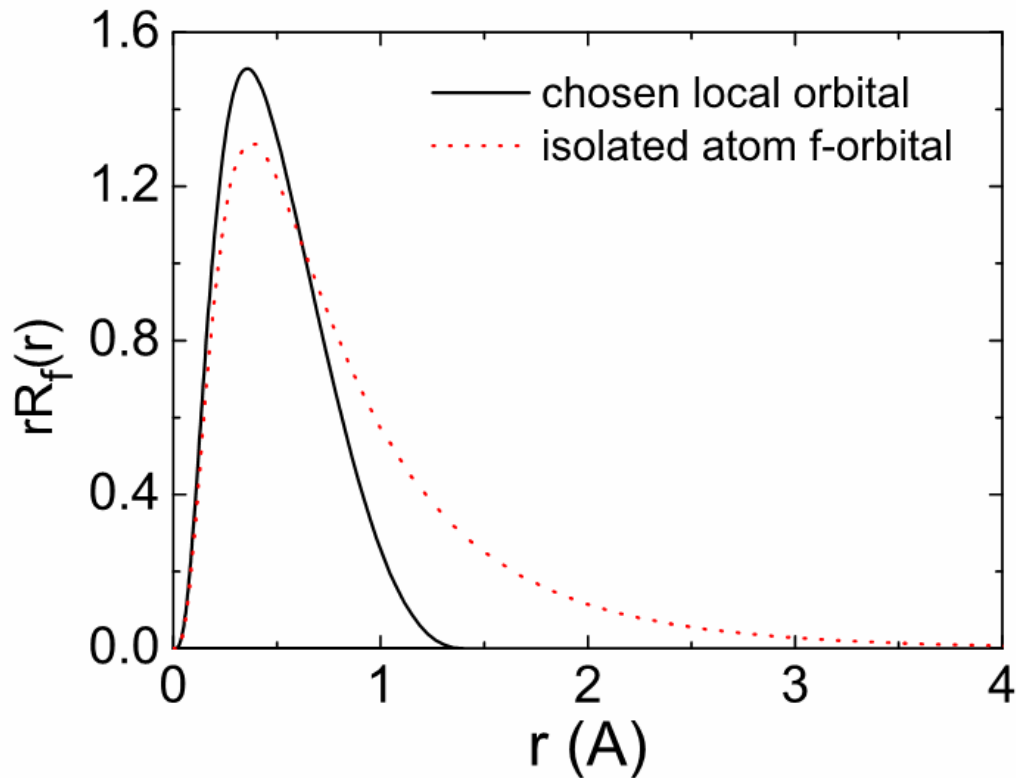
	a_0 (Å)	B (GPa)
LDA	4.52	57.4
G-DFT	4.88	34.7
Expt.	4.83	27.0

Gutzwiller-LDA shows better agreement with experiment

Critique

- Results may be sensitive to choice of local basis
→ Need to optimize local basis during self-consistency (Work in progress)

Application (Ce)



Simple choice: truncated free f-wavefunction as our local orbital

Summary

- Developed a new density functional incorporating correlated electronic effects into the kinetic energy via the Gutzwiller approximation
- First principles formulation: all Coulomb integrals determined self-consistently, no adjustable parameters
- A preliminary Fortran90 code has been developed with an interface to VASP
- Preliminary application to FCC Ce.

Thank you