Gutzwiller Density Functional Theory

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Electronic many-particle Hamiltonian ($\sigma = \uparrow, \downarrow; \hbar \equiv 1$)

$$\hat{H} = \hat{H}_{\text{band}} + \hat{H}_{\text{int}},$$

$$\hat{H}_{\text{band}} = \sum_{\sigma} \int d\mathbf{r} \hat{\Psi}_{\sigma}^{\dagger}(\mathbf{r}) \left( -\frac{\Delta}{2m} + U(\mathbf{r}) \right) \hat{\Psi}_{\sigma}(\mathbf{r}), \quad (1)$$

$$\hat{H}_{\text{int}} = \sum_{\sigma, \sigma'} \int d\mathbf{r} \int d\mathbf{r}' \hat{\Psi}_{\sigma}^{\dagger}(\mathbf{r}) \hat{\Psi}_{\sigma'}^{\dagger}(\mathbf{r}') V(\mathbf{r} - \mathbf{r}') \hat{\Psi}_{\sigma'}(\mathbf{r}') \hat{\Psi}_{\sigma}(\mathbf{r}).$$

The electrons experience their mutual Coulomb interaction and the interaction with the ions at positions $\mathbf{R}$,

$$V(\mathbf{r} - \mathbf{r}') = \frac{1}{2} \frac{e^2}{|\mathbf{r} - \mathbf{r}'|}, \quad U(\mathbf{r}) = \sum_{\mathbf{R}} \frac{e^2}{|\mathbf{r} - \mathbf{R}|} \quad (2)$$
The many-body problem in solid-state theory

Objective

Explain all fascinating phenomena in solid-state physics, e.g., magnetism and superconductivity.
To this end, solve the Schrödinger equation, $\hat{H}|\psi_n\rangle = E_n|\psi_n\rangle$, and calculate all expectation values of interest, $A_{n,m} = \langle \psi_n | \hat{A} | \psi_m \rangle$.

Problems

- $\hat{H}$ poses an extremely difficult many-body problem.
- The bare energy scales are of the order of ten electron Volt (eV) per unit cell, the energy scales of interest (10 K) are milli-eV (relative accuracy requirement $10^{-4}$, or better).
The many-body problem in solid-state theory

‘Solution’

- Focus on simpler Hamiltonians (e.g., Heisenberg or Hubbard models) and their ground-state properties;
- Design sensible approximations for models and/or for $\hat{H}$, e.g., the Local Density Approximation (LDA) to Density Functional Theory (DFT).

In this lecture, you will learn that

- The Gutzwiller Density Functional Theory provides an approximate description of the many-particle ground state of the electronic problem, and of its elementary Landau quasi-particle excitations.
- At its core, it provides an approximate ground state for the multi-band Hubbard model with its purely local interactions.
Outline of Part I

1 Hubbard model
   - Hamiltonian
   - Problems
   - Multi-band Hubbard model

2 Gutzwiller variational states
   - Definition
   - Application to the two-site Hubbard model

3 Evaluation in high dimensions
   - Limit of high dimensions
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4 Summary of part I
Outline of Part II

5 Density Functional Theory
   • Electronic problem
   • Levy’s constrained search
   • Single-particle Hamiltonian and Ritz variational principle
   • Kohn-Sham equations

6 Density Functional Theory for many-particle Hamiltonians
   • Hubbard interaction and Hubbard density functional
   • Gutzwiller density functional
   • Limit of infinite lattice coordination number

7 Transition metals
   • Gutzwiller–Kohn-Sham quasi-particle Hamiltonian
   • Local Hamiltonian for transition metals
   • Results for nickel
   • Results for iron

8 Summary of part II
Part I

Gutzwiller variational approach
Hubbard model: a toy model for interacting electrons
(see talk by R. Eder)

Fig. 1: Electrons with spin $\sigma = \uparrow, \downarrow$ on a lattice

Kinetic term

$$\hat{T} = \sum_{\mathbf{R}, \mathbf{R}'; \sigma} t_{\mathbf{R}-\mathbf{R}'} \hat{c}^+_{\mathbf{R}, \sigma} \hat{c}_{\mathbf{R}', \sigma}$$  \(3\)

$t_{\mathbf{R}-\mathbf{R}'}$: electron transfer amplitude from lattice site $\mathbf{R}'$ to $\mathbf{R}$

Hubbard interaction

$$\hat{V} = U \sum_{\mathbf{R}} \hat{n}_{\mathbf{R}, \uparrow} \hat{n}_{\mathbf{R}, \downarrow}$$  \(4\)

$U$: strength of the Coulomb repulsion

Single-band Hubbard Hamiltonian

$$\hat{H} = \hat{T} + \hat{V}$$  \(5\)
Technical problems

- The Hubbard model poses an extremely difficult many-body problem (see talk by R. Eder)!
- (Asymptotic) Bethe Ansatz provides the exact solution in one dimension for $t_\kappa(r) \sim \sinh(\kappa)/\sinh(\kappa r)$.
- In the limit of infinite dimensions, the model can be mapped onto an effective single-impurity Anderson model whose dynamics must be determined self-consistently (Dynamical Mean-Field Theory, see talks by E. Pavarini and V. Janiš).

Conceptual problem

The single-band Hubbard model is too simplistic for the description of real materials, e.g., of the 3d-electrons in transition metals.
Hubbard model: a toy model for interacting electrons

Minimal extension: multi-band Hubbard model (orbital index $b$)

\[
\hat{H} = \sum_{R,R';\sigma} t^b_{R-R'} \hat{c}^{+}_{R,b,\sigma} \hat{c}_{R',b,\sigma} \\
+ \sum_{R} \sum_{b_1,...,b_4; \sigma_1,...,\sigma_4} U^{b_3\sigma_3,b_4\sigma_4}_{b_1\sigma_1,b_2\sigma_2} \hat{c}^{+}_{R,b_1,\sigma_1} \hat{c}^{+}_{R,b_2,\sigma_2} \hat{c}_{R,b_3,\sigma_3} \hat{c}_{R,b_4,\sigma_4}
\] (6)

Problem

The multi-band Hubbard model is not exactly solvable. It readily exceeds our numerical capabilities even in DMFT when more than three bands are involved.

'Solution'

Use variational many-particle states as approximate ground states. In the following: we use Gutzwiller variational states.
Gutzwiller variational state

Observation for the single-band Hubbard model: doubly occupied sites are unfavorable for the potential energy ($U > 0$).

Gutzwiller’s Ansatz for the single-band Hubbard model

\[
|\psi_G\rangle = \hat{P}_G |\phi\rangle, \quad \hat{P}_G = g \hat{D},
\]

where

- $|\psi_G\rangle$: Gutzwiller variational state
- $|\phi\rangle$: single-particle product state, e.g., the Fermi sea
- $\hat{P}_G$: Gutzwiller correlator
- $g$: real variational parameter
- $\hat{D} = \sum_R \hat{n}_{R,\uparrow} \hat{n}_{R,\downarrow}$: number of doubly occupied sites

The Gutzwiller variational state is exact for $U = 0$ (free Fermions), and for $U = \infty$ (no double occupancies).
Gutzwiller variational state

For the multi-band Hubbard model and for \( t_{R-R'} \equiv 0 \), we must work with the atomic eigenstates \( |\Gamma\rangle \) of \( \hat{V} \),

\[
\hat{V} = \sum_{b_1,\ldots,b_4; \sigma_1,\ldots,\sigma_4} U^{b_3 \sigma_3, b_4 \sigma_4}_{b_1 \sigma_1, b_2 \sigma_2} \hat{c}_{b_1,\sigma_1} \hat{c}_{b_2,\sigma_2} \hat{c}_{b_3,\sigma_3} \hat{c}_{b_4,\sigma_4} = \sum_{R;\Gamma} E_{R;\Gamma} \hat{m}_{R;\Gamma} \quad (8)
\]

where \( \hat{m}_{R;\Gamma} = |\Gamma_R\rangle \langle \Gamma_R| = \hat{m}_{R;\Gamma}^2 \) projects onto the atomic eigenstate \( |\Gamma\rangle \) on site \( R \).

Gutzwiller Ansatz for the multi-band Hubbard model

\[
|\psi_G\rangle = \hat{P}_G |\Phi\rangle \quad , \quad \hat{P}_G = \prod_R \prod_{\Gamma_R} \lambda_{R;\Gamma}^{\hat{m}_{R;\Gamma}} = \prod_R \sum_{\Gamma_R} \lambda_{R;\Gamma} \hat{m}_{R;\Gamma} \quad , \quad (9)
\]

where

- \( |\psi_G\rangle \): Gutzwiller variational state
- \( \lambda_{R;\Gamma} \): real variational parameter
- \( |\Phi\rangle \): single-particle product state, e.g., the Fermi sea
Gutzwiller variational state

The ground state of the two-site Hubbard model with tunnel amplitude \((-t)\) and \(N_\uparrow = N_\downarrow = L/2 = 1\) electrons is given in position space by

\[
|\Psi_0\rangle \sim (|\uparrow_1, \downarrow_2\rangle - |\downarrow_1, \uparrow_2\rangle) + \alpha(U/t)(|\uparrow_1, \emptyset_2\rangle + |\emptyset_1, \uparrow_2\rangle)
\]

with \(\alpha(x) = (x - \sqrt{x^2 + 16})/4\) and \(E_0(U) = -2t\alpha(U/t)\).

The Gutzwiller-correlated Fermi sea has the form

\[
|\Psi_G\rangle \sim (|\uparrow_1, \downarrow_2\rangle - |\downarrow_1, \uparrow_2\rangle) + g(|\uparrow_1, \emptyset_2\rangle + |\emptyset_1, \uparrow_2\rangle)
\]

Ritz’s variational principle thus gives \(g^{\text{opt}} = \alpha(U/t)\): exact!

Problem

The evaluation of expectation values with Gutzwiller variational states poses a very difficult many-body problem.
Evaluation in high dimensions

Let $Z$ be the number of nearest neighbors of a lattice site, e.g., $Z = 2d$ for a simple-cubic lattice in $d$ dimensions.

**Question**

How do we have to scale the electron transfer matrix element between nearest neighbors in the limit $Z \to \infty$?

For the spin-1/2 Ising model we have to scale

$$J = \frac{J^*}{Z} \quad (J^* = \text{const}) \quad (12)$$

because each of the $Z$ neighbors can contribute the energy $J^*/4$.

At large interactions $U$, the Hubbard at half band-filling maps onto the Heisenberg model with $J = J^*/Z \sim t^2/U$. Thus, we scale

$$t \sim t^*/\sqrt{Z} \quad (13)$$
Evaluation in high dimensions

Expectation values with the Gutzwiller variational state are calculated using diagrammatic perturbation theory. Lines that connect lattice sites \( R \) and \( R' \) represent the single-particle density matrix,

\[
P^0_\sigma(R, b; R', b') = \langle \Phi | \hat{c}^+_R, b, \sigma \hat{c}_{R', b', \sigma} | \Phi \rangle \sim \left( \frac{1}{Z} \right)^{\|R-R'\|/2}. \tag{14}
\]

Collapse of diagrams in position space

When two inner vertices \( f_1 \) and \( f_2 \) are connected by three different paths, we may set \( f_1 = f_2 \) in the limit \( Z \to \infty \) because the summation over \( Z^{\|f_1-f_2\|} \) neighbors cannot compensate the factor \( Z^{-3\|f_1-f_2\|/2} \) from the three lines for \( f_1 \neq f_2 \).

How can we get rid of the remaining local contributions?
Diagrammatic expansion for Gutzwiller states

1. Develop a diagrammatic perturbation theory with vertices $x_{f,l_1,l_2}$ and lines $\tilde{P}_\sigma^0(f_1, b_1; f_2, b_2)$;

2. Choose the expansion parameters $x_{f,l_1,l_2}$ such that
   - at least four lines meet at every inner vertex,
   - there are no Hartree bubble diagrams, and
   - the single-particle density matrices vanish on the same site,

   $$\tilde{P}_\sigma^0(f, b; f, b') = 0 ; \quad (15)$$

3. In the limit $Z \rightarrow \infty$, all skeleton diagrams collapse in position space, i.e., they have the same lattice site index. As a consequence of Eq. (15), they all vanish and not a single diagram with inner vertices must be calculated.
We use the representation ($\hat{P}_G = \prod_f \hat{P}_{G,f}$)
\[
\hat{P}_{G,f}^2 = 1 + x_f (\hat{n}_{f,\uparrow} - \langle \hat{n}_{f,\uparrow} \rangle \Phi)(\hat{n}_{f,\downarrow} - \langle \hat{n}_{f,\downarrow} \rangle \Phi) .
\]
(16)

Note: the Hartree contributions are eliminated by construction, there are only inner vertices vertices with four lines.

Now that we also have ($\hat{P}_{G,f} = \sum \lambda_{f;\Gamma} \hat{m}_{f;\Gamma}$)
\[
\hat{P}_{G,f}^2 = \lambda_{f;\emptyset}^2 (1 - \hat{n}_{f,\uparrow})(1 - \hat{n}_{f,\downarrow}) + \lambda_{f;\uparrow\downarrow} \hat{n}_{f,\uparrow} \hat{n}_{f,\downarrow}
+ \lambda_{f;\uparrow}^2 \hat{n}_{f,\uparrow}(1 - \hat{n}_{f,\downarrow}) + \lambda_{f;\downarrow}^2 (1 - \hat{n}_{f,\uparrow}) \hat{n}_{f,\downarrow} ,
\]
(17)

so that we know $\lambda_{f;\emptyset}$, $\lambda_{f;\sigma}$ and $\lambda_{f;\uparrow\downarrow}$ as a function of $x_f$.

In infinite dimensions ($R \neq R'$)
\[
\langle \hat{n}_{R,\uparrow} \hat{n}_{R,\downarrow} \rangle_G = \lambda_{R;\uparrow\downarrow}^2 \langle \hat{n}_{R,\uparrow} \rangle \Phi \langle \hat{n}_{R,\downarrow} \rangle \Phi ,
\]
\[
\langle \hat{c}_{R,\sigma}^+ \hat{c}_{R',\sigma} \rangle_G = q_{R,\sigma} q_{R',\sigma} \langle \hat{c}_{R,\sigma}^+ \hat{c}_{R',\sigma} \rangle \Phi .
\]
(18)

$q_{R,\sigma}$ is a known function of $x_R$. 

Note: the Hartree contributions are eliminated by construction, there are only inner vertices vertices with four lines.
Evaluation in high dimensions

For the Hubbard model with nearest-neighbor transfer \((-t)\) at half band-filling and for a Gutzwiller-correlated paramagnetic Fermi sea, we have to optimize

\[
E_{\text{var}} = \langle \Phi | \hat{H}_{0}^{\text{eff}} | \Phi \rangle + UL\lambda_{\uparrow\downarrow}^2, \quad \hat{H}_{0}^{\text{eff}} = \sum_{k} \left[ q^2\epsilon(k) \right] \hat{n}_{k;\sigma}
\]  

(19)

with respect to \(\lambda_{\uparrow\downarrow}\) where \(0 \leq q^2 = \lambda_{\uparrow\downarrow}^2 (2 - \lambda_{\uparrow\downarrow}^2) \leq 1\).

Brinkman-Rice (BR) metal-to-insulator transition

\[
\langle \hat{D}/L \rangle_G = \frac{\lambda_{\uparrow\downarrow}^2}{4} = \frac{1}{4} \left( 1 - \frac{U}{U_{BR}} \right), \quad q^2 = 1 - \left( \frac{U}{U_{BR}} \right)^2.
\]

(20)

All particles are localized beyond \(U_{BR} = 8|\langle \hat{T} \rangle_0/L|\) (BR insulator).
Evaluation in high dimensions

Quasi-particle picture

The single-particle Hamiltonian $H_0^{\text{eff}}$ describes quasi-particles.

- Landau’s idea of quasi-particles
  Fermi gas + hole exc. $\rightarrow$ Fermi liquid + quasi-hole exc.

- Realization in terms of Gutzwiller wave functions
  Fermi-gas ground state: $|\Phi\rangle = \prod_{\mathbf{p},\sigma;\epsilon(p)\leq E_F} \hat{h}_{\mathbf{p},\sigma}^+ |\text{vac}\rangle$
  Fermi-liquid ground state: $|\Psi_G\rangle = \hat{P}_G |\Phi\rangle$
  hole excitation: $\hat{h}_{\mathbf{p},\sigma} |\Phi\rangle$
  quasi-hole excitation: $|\Psi_{G;\mathbf{p},\sigma}\rangle = \hat{P}_G \hat{h}_{\mathbf{p},\sigma} |\Phi\rangle$

- Energy of Landau-Gutzwiller quasi-particles

$$E_{\sigma}^{\text{QP}}(\mathbf{p}) := \frac{\langle \Psi_{G;\mathbf{p},\sigma} | \hat{H} | \Psi_{G;\mathbf{p},\sigma} \rangle}{\langle \Psi_{G;\mathbf{p},\sigma} | \Psi_{G;\mathbf{p},\sigma} \rangle} - E_0^{\text{var}} \overset{Z=\infty}{=} \tilde{\epsilon}_{\sigma}(\mathbf{p}) \quad (21)$$

$\tilde{\epsilon}_{\sigma}(\mathbf{p})$: dispersion relation of $\hat{H}_0^{\text{eff}}$; here: $\tilde{\epsilon}_{\sigma}(\mathbf{p}) = q^2 \epsilon(\mathbf{p})$. 
What have we discussed so far?

Gutzwiller-correlated single-particle states are approximate ground states for (multi-band) Hubbard models.

- **Formalism:**
  - Gutzwiller wave functions are evaluated in an elegant diagrammatic formalism where Hartree bubbles are absent and lines connect only different inner vertices.
  - In the limit of infinite coordination number, $Z \to \infty$, diagrams with inner vertices are zero.

- **Application:**
  - The Gutzwiller theory is a concrete example for Landau’s Fermi-liquid picture.
  - The Gutzwiller theory provides dispersion relations for Landau-Gutzwiller quasi-particles.
Part II

Combination with Density Functional Theory
Density Functional Theory

Reminder: Electronic many-particle Hamiltonian \((\sigma = \uparrow, \downarrow; \hbar \equiv 1)\)

\[
\hat{H} = \hat{H}_{\text{band}} + \hat{H}_{\text{int}},
\]

\[
\hat{H}_{\text{band}} = \sum_{\sigma} \int \text{d}r \hat{\Psi}_{\sigma}^{\dagger}(r) \left( -\frac{\Delta_r}{2m} + U(r) \right) \hat{\Psi}_{\sigma}(r), \quad (22)
\]

\[
\hat{H}_{\text{int}} = \sum_{\sigma, \sigma'} \int \text{d}r \int \text{d}r' \hat{\Psi}_{\sigma}^{\dagger}(r) \hat{\Psi}_{\sigma'}^{\dagger}(r') V(r - r') \hat{\Psi}_{\sigma'}(r') \hat{\Psi}_{\sigma}(r).
\]

The electrons experience their mutual Coulomb interaction and the interaction with the ions at positions \(\mathbf{R}\),

\[
V(r - r') = \frac{1}{2} \frac{e^2}{|r - r'|}, \quad U(r) = \sum_{\mathbf{R}} \frac{e^2}{|r - \mathbf{R}|}, \quad (23)
\]
Density Functional Theory

Ritz variational principle

Task: minimize the energy functional

\[ E \left[ \{ | \Psi \rangle \} \right] = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle}. \]  \hspace{1cm} (24)

Problem

This task poses an extremely difficult many-body problem!

Density Functional Theory (see talk by R. Martin)

Express the energy functional in terms of a density functional – and make some educated approximations later in the game!
Consider all normalized states $|\Psi^{(n)}\rangle$ for given ‘physical’ densities

\[ n_\sigma(r) = \langle \Psi^{(n)} | \hat{\Psi}^\dagger_\sigma(r) \hat{\Psi}_\sigma(r) | \Psi^{(n)} \rangle. \quad (25) \]

The purely electronic operator $\hat{H}_e = \hat{H}_{\text{kin}} + \hat{V}_{\text{xc}}$ (kinetic energy + exchange-correlation energy) is

\[
\hat{H}_{\text{kin}} = \sum_\sigma \int dr \hat{\Psi}^\dagger_\sigma(r) \left( -\frac{\Delta r}{2m} \right) \hat{\Psi}_\sigma(r), \quad (26)
\]

\[
\hat{V}_{\text{xc}} = \sum_{\sigma, \sigma'} \int dr \int dr' V(r - r') \left[ \hat{\Psi}^\dagger_\sigma(r) \hat{\Psi}^\dagger_{\sigma'}(r') \hat{\Psi}_{\sigma'}(r') \hat{\Psi}_\sigma(r) 
\right.
\]
\[ - 2 \hat{\Psi}^\dagger_\sigma(r) \hat{\Psi}_\sigma(r) n_{\sigma'}(r') + n_\sigma(r) n_{\sigma'}(r') \].

For fixed densities, the interaction with the ions and the Hartree interaction are constant.
Density Functional Theory

### Levy’s constraint search

Task: minimize the energy functional

\[
F \left[ \{ n_\sigma(r) \} , \{ |\psi^{(n)}\rangle \} \right] = \langle \psi^{(n)} | \hat{H}_{\text{kin}} + \hat{V}_{\text{xc}} | \psi^{(n)} \rangle . \quad (27)
\]

for fixed densities \( n_\sigma(r) \). Result: optimized \( |\psi_0^{(n)}\rangle \). 

### Density functionals for the kinetic/exchange-correlation energy

We define two energy functionals that only depend on the densities,

**Kinetic:**

\[
K \left[ \{ n_\sigma(r) \} \right] = \langle \psi_0^{(n)} | \hat{H}_{\text{kin}} | \psi_0^{(n)} \rangle , \quad (28)
\]

**Exchange-correlation:**

\[
E_{\text{xc}} \left[ \{ n_\sigma(r) \} \right] = \langle \psi_0^{(n)} | \hat{V}_{\text{xc}} | \psi_0^{(n)} \rangle . \quad (29)
\]
Density Functional Theory

Density Functional

Task: minimize the Density Functional

\[ D \left[ \{ n_\sigma(r) \} \right] = K \left[ \{ n_\sigma(r) \} \right] + E_{xc} \left[ \{ n_\sigma(r) \} \right] + U \left[ \{ n_\sigma(r) \} \right] + V_{Har} \left[ \{ n_\sigma(r) \} \right] \] (30)

with the ionic/Hartree energies

Ionic: \[ U \left[ \{ n_\sigma(r) \} \right] = \sum_\sigma \int d\mathbf{r} U(r)n_\sigma(r) , \] (31)

Hartree: \[ V_{Har} \left[ \{ n_\sigma(r) \} \right] = \sum_{\sigma,\sigma'} \int d\mathbf{r} \int d\mathbf{r}' V(\mathbf{r} - \mathbf{r}')n_\sigma(r)n_{\sigma'}(r') . \]

The minimization provides the ground-state densities \( n_\sigma^0(r) \) and the ground-state energy \( E_0 = D \left[ \{ n_\sigma^0(r) \} \right] \).
Problem
The minimization of the energy functional in eq. (27) poses an extremely difficult many-particle problem. Thus, the exact density functional $D \{n_\sigma(r)\}$ is unknown.

Hohenberg-Kohn approach
Idea: derive the same ground-state physics from an effective single-particle problem.

How can this be achieved?
In the following we follow a simple and straightforward strategy, not the most general one (see talk by R. Martin).
Density Functional Theory

Consider all normalized single-particle product states $|\Phi^{(n)}\rangle$ for given ‘physical’ densities

$$n_{\sigma}^{sp}(r) = \langle \Phi^{(n)} | \hat{\Psi}_\sigma^\dagger(r) \hat{\Psi}_\sigma(r) | \Phi^{(n)} \rangle .$$  \hspace{1cm} (32)

As our single-particle Hamiltonian we consider the kinetic-energy operator $\hat{H}_{\text{kin}}$. For fixed single-particle densities $n_{\sigma}^{sp}(r)$, we define the single-particle functional

$$F_{\text{sp}} \left[ \{ n_{\sigma}^{sp}(r) \} , \left\{ |\Phi^{(n)}\rangle \right\} \right] = \langle \Phi^{(n)} | \hat{H}_{\text{kin}} | \Phi^{(n)} \rangle .$$  \hspace{1cm} (33)

Levy’s constrained search provides the optimized $|\Phi_0^{(n)}\rangle$ and

$$K_{\text{sp}} \left[ \{ n_{\sigma}^{sp}(r) \} \right] = \langle \Phi_0^{(n)} | \hat{H}_{\text{kin}} | \Phi_0^{(n)} \rangle .$$  \hspace{1cm} (34)
Density Functional Theory

The single-particle density functional is defined as

\[
D_{\text{sp}} \{n^{\text{sp}}_{\sigma}(r)\} = K_{\text{sp}} \{n^{\text{sp}}_{\sigma}(r)\} + U \{n^{\text{sp}}_{\sigma}(r)\} + V_{\text{Har}} \{n^{\text{sp}}_{\sigma}(r)\} + E_{\text{sp,xc}} \{n^{\text{sp}}_{\sigma}(r)\}
\]  

(35)

with the yet unspecified single-particle exchange-correlation energy \(E_{\text{sp,xc}} \{n^{\text{sp}}_{\sigma}(r)\}\).

Assumption: non-interacting \(V\)-representability

For any given (physical) densities \(n_{\sigma}(r)\) we can find normalized single-particle product states \(|\Phi^{(n)}\rangle\) such that

\[
n^{\text{sp}}_{\sigma}(r) = n_{\sigma}(r).
\]  

(36)
Hohenberg-Kohn theorem

We demand

\[ D_{\text{sp}} \left[ \{ n_\sigma(r) \} \right] = D \left[ \{ n_\sigma(r) \} \right]. \] (37)

⇒ The single-particle substitute system has the same ground-state density \( n^0_\sigma(r) \) and energy \( E_0 \) as the many-particle Hamiltonian.

Single-particle exchange-correlation energy

To fulfill eq. (37), we define

\[ E_{\text{sp,xc}} \left[ \{ n_\sigma(r) \} \right] = K \left[ \{ n_\sigma(r) \} \right] - K_{\text{sp}} \left[ \{ n_\sigma(r) \} \right] + E_{\text{xc}} \left[ \{ n_\sigma(r) \} \right]. \] (38)

Problem

We know neither of the quantities on the r.h.s. of eq. (38)!
Upshot of the Hohenberg-Kohn theorem:

- A single-particle substitute system exists that leads to the exact ground-state properties.
- Its energy functional takes the form

\[
E \left[ \{ n_\sigma(r) \} , \{ |\Phi\rangle \} \right] = \langle \Phi | \hat{H}_{\text{kin}} |\Phi\rangle + U \left[ \{ n_\sigma(r) \} \right] \\
+ V_{\text{Har}} \left[ \{ n_\sigma(r) \} \right] + E_{\text{sp,xc}} \left[ \{ n_\sigma(r) \} \right].
\] (39)

Remaining task:

minimize \( E \left[ \{ n_\sigma(r) \} , \{ |\Phi\rangle \} \right] \) in the subset of single-particle product states \(|\Phi\rangle = \prod_{n,\sigma} ^{'} \hat{b}^\dagger_{n,\sigma} |\text{vac}\rangle \). The field operators are expanded as

\[
\hat{\Psi}^\dagger_\sigma(r) = \sum_n \psi^*_n(r) \hat{b}^\dagger_{n,\sigma}, \quad \hat{\Psi}_\sigma(r) = \sum_n \psi_n(r) \hat{b}_{n,\sigma}.
\] (40)
Density Functional Theory

With the Hartree and exchange-correlation potentials

\[ V_{\text{Har}}(r) \equiv \sum_{\sigma'} \int \, dr' 2V(r - r') n_{\sigma'}^0(r') , \]

\[ v_{\text{sp},\text{xc},\sigma}(r) \equiv \left. \frac{\partial E_{\text{sp},\text{xc}}[\{n_{\sigma'}(r')\}]}{\partial n_{\sigma}(r)} \right|_{n_{\sigma}(r) = n_{\sigma}^0(r)} , \tag{41} \]

the minimization conditions lead to the Kohn-Sham equations.

Kohn-Sham equations

\[ h_{\sigma}^{\text{KS}}(r) \psi_n(r) = \epsilon_n(r) \psi_n(r) , \]

\[ h_{\sigma}^{\text{KS}}(r) \equiv -\frac{\Delta r}{2m} + V_{\sigma}^{\text{KS}}(r) , \tag{42} \]

\[ V_{\sigma}^{\text{KS}}(r) \equiv U(r) + V_{\text{Har}}(r) + v_{\text{sp},\text{xc},\sigma}(r) . \]
Resume of DFT

- There exists a single-particle substitute system that has the same ground-state energy and ground-state densities as the interacting many-electron system.
- If we knew the single-particle exchange-correlation energy $E_{\text{sp,xc}} \{n_\sigma(r)\}$, the Kohn-Sham equations would provide single-particle eigenstates that define the single-particle ground state $|\Phi_0\rangle$. The exact ground-state properties can be extracted from $|\Phi_0\rangle$.

Remaining task

Find physically reasonable approximations for $E_{\text{sp,xc}} \{n_\sigma(r)\}$. Example: the local (spin) density approximation (L(S)DA).
Limitations of DFT-L(S)DA & Co

The properties of transition metals and their compounds are not so well described.
Reason: $3d$ electrons are strongly correlated.

Solution

Treat interaction of electrons in correlated bands separately!
The kinetic energy $\hat{H}_{\text{kin}}$ plus the Hubbard interaction $\hat{V}_{\text{loc}}$ define our new reference system,

$$\hat{H}_{\text{kin}} \rightarrow \hat{H}_{\text{H}} = \hat{H}_{\text{kin}} + \hat{V}_{\text{loc}} - \hat{V}_{\text{dc}}.$$  \hfill (43)

Here, $\hat{V}_{\text{dc}}$ accounts for the double counting of the Coulomb interactions among correlated electrons.
Density Functional Theory for many-particle Hamiltonians

Using the same formalism as before, we define the functional
\[
F_H \left[ \{ n_\sigma (r) \} , \left\{ | \psi^{(n)} \rangle \right\} \right] = \langle \psi^{(n)} | \hat{H}_H | \psi^{(n)} \rangle . \tag{44}
\]

Its optimization provides \( | \psi^{(n)}_{H,0} \rangle \) and the functionals
\[
K_H \left[ \{ n_\sigma (r) \} \right] = \langle \psi^{(n)}_{H,0} | \hat{H}_{\text{kin}} | \psi^{(n)}_{H,0} \rangle ,
\]
\[
V_{\text{loc/dc}} \left[ \{ n_\sigma (r) \} \right] = \langle \psi^{(n)}_{H,0} | \hat{V}_{\text{loc/dc}} | \psi^{(n)}_{H,0} \rangle , \tag{45}
\]
\[
D_H \left[ \{ n_\sigma (r) \} \right] = K_H \left[ \{ n_\sigma (r) \} \right] + U \left[ \{ n_\sigma (r) \} \right] + V_{\text{Har}} \left[ \{ n_\sigma (r) \} \right] + V_{\text{loc}} \left[ \{ n_\sigma (r) \} \right] - V_{\text{dc}} \left[ \{ n_\sigma (r) \} \right] + E_{H,xc} \left[ \{ n_\sigma (r) \} \right] . \tag{46}
\]

We demand \( D_H \left[ \{ n_\sigma (r) \} \right] = D \left[ \{ n_\sigma (r) \} \right] \). Then, \( \hat{H}_H \) leads to the exact ground-state energy \( E_0 \) and densities \( n^{0}_\sigma (r) \).
Density Functional Theory for many-particle Hamiltonians

Problem

The Hubbard interaction $\hat{V}_{\text{loc}}$ reintroduces the complexity of the full many-body problem! – What have we gained?

Indeed, when we apply the Ritz principle to the energy functional

$$E = \langle \Psi | \hat{H}_H | \Psi \rangle + U \left[ \{ n_\sigma (r) \} \right] + V_{\text{Har}} \left[ \{ n_\sigma (r) \} \right] + E_{H, xc} \left[ \{ n_\sigma (r) \} \right],$$

we arrive at the many-particle Hubbard-Schrödinger equation

$$\left( \hat{H}_0 + \hat{V}_{\text{loc}} - \hat{V}_{\text{dc}} \right) | \Psi_0 \rangle = E_0 | \Psi_0 \rangle$$

with the single-particle Hamiltonian

$$\hat{H}_0 = \sum_\sigma \int \! \! \! \! \! dr \hat{\Psi}^{\dagger}_\sigma (r) \left( -\frac{\Delta r}{2m} + U(r) + V_{\text{Har}}(r) + v_{H, xc, \sigma}(r) \right) \hat{\Psi}_\sigma (r).$$
Density Functional Theory for many-particle Hamiltonians

Advantage

Local interactions among correlated electrons are treated explicitly so that they are subtracted from the exact exchange-correlation energy,

\[
E_{H,\text{xc}} \left[ \{ n_\sigma(r) \} \right] = K \left[ \{ n_\sigma(r) \} \right] - K_H \left[ \{ n_\sigma(r) \} \right] + E_{\text{xc}} \left[ \{ n_\sigma(r) \} \right] - (V_{\text{loc}} \left[ \{ n_\sigma(r) \} \right] - V_{\text{dc}} \left[ \{ n_\sigma(r) \} \right]) \quad (50)
\]

Consequence: an (L(S)DA) approximation should better suited for \( E_{H,\text{xc}} \) than for \( E_{\text{sp,xc}} \).

Later, we shall employ the approximation

\[
E_{H,\text{xc}} \left[ \{ n_\sigma(r) \} \right] \approx E_{\text{LDA,xc}} \left[ \{ n_\sigma(r) \} \right] \quad (51)
\]
Approximate treatments

Idea: approximate the functional \( \langle \Psi | \hat{H}_{\text{kin}} + \hat{V}_{\text{loc}} - \hat{V}_{\text{dc}} | \Psi \rangle \).

Strategies:

- Limit of infinite dimensions: use DMFT to determine \( |\Psi\rangle \).
- LDA+U: use single-particle variational states \( |\Phi\rangle \).
- Gutzwiller: use many-particle variational states \( |\Psi_G\rangle \).

Consider atomic states \( |\Gamma_R\rangle \) at lattice site \( R \) that are built from the correlated orbitals. With the local many-particle operators \( \hat{m}_{R;\Gamma} = |\Gamma_R\rangle \langle \Gamma_R| \) we define the Gutzwiller states as in part I

\[
|\Psi_G\rangle = \hat{P}_G |\Phi\rangle \quad , \quad \hat{P}_G = \prod_R \sum_\Gamma \lambda_{R;\Gamma} \hat{m}_{R;\Gamma}.
\]

(52)

\( \lambda_{R;\Gamma} \) are real variational parameters.
The energy functional requires the evaluation of expectation values for the local interaction

\[
V_{\text{loc}/d\text{c}} = \sum_{\mathbf{R}} \sum_{\Gamma, \Gamma'} E_{\Gamma, \Gamma'}^{\text{loc}/d\text{c}} (\mathbf{R}) \frac{\langle \Psi_G | \hat{m}_{\mathbf{R}; \Gamma, \Gamma'} | \Psi_G \rangle}{\langle \Psi_G | \Psi_G \rangle}, \quad (53)
\]

\[
E_{\Gamma, \Gamma'}^{\text{loc}/d\text{c}} (\mathbf{R}) = \langle \Gamma_{\mathbf{R}} | \hat{V}_{\text{loc}/d\text{c}} (\mathbf{R}) | \Gamma'_{\mathbf{R}} \rangle, \quad (54)
\]

and for the single-particle density matrix, e.g., in the orbital Wannier basis \((\hat{\Psi}_\sigma (\mathbf{r}) = \sum_{\mathbf{R}} \phi_{\mathbf{R}, b, \sigma} (\mathbf{r}) \hat{c}_{\mathbf{R}, b, \sigma})\),

\[
\rho^{G}_{(\mathbf{R}', b'), (\mathbf{R}, b); \sigma} = \frac{\langle \Psi_G | \hat{c}_{\mathbf{R}, b, \sigma}^\dagger \hat{c}_{\mathbf{R}', b', \sigma} | \Psi_G \rangle}{\langle \Psi_G | \Psi_G \rangle}. \quad (55)
\]
The Gutzwiller energy functional $E \equiv E \left[ \{ n_\sigma (r) \} , \{ |\Psi_G\rangle \} \right]$ reads

$$E = \sum_{R,b,R',b',\sigma} T_{(R,b),(R',b');\sigma} \rho_G^{(R',b'),(R,b);\sigma} + V_{\text{loc}}^G - V_{\text{dc}}^G$$

$$+ U \left[ \{ n_\sigma (r) \} \right] + V_{\text{Har}} \left[ \{ n_\sigma (r) \} \right] + E_{\text{H,xc}} \left[ \{ n_\sigma (r) \} \right], \quad (56)$$

$$T_{(R,b),(R',b');\sigma} = \int \text{d}r \phi_{R,b,\sigma}^*(r) \left( -\frac{\Delta r}{2m} \right) \phi_{R',b',\sigma}(r). \quad (57)$$

The densities become

$$n_\sigma (r) = \sum_{R,b,R',b'} \phi_{R,b,\sigma}^*(r) \phi_{R',b',\sigma}(r) \rho_G^{(R',b'),(R,b);\sigma}. \quad (58)$$
Problem

The evaluation of expectation values with Gutzwiller-correlated states poses an extremely difficult many-particle problem.

Solution (see part I)

Evaluate expectation values diagrammatically in such a way that not a single diagram must be calculated in the limit of infinite lattice coordination number, \( Z \to \infty \) (recall: \( Z = 12 \) for nickel).

Result: all quantities depend only on the single-particle density matrix \( C_{b',b;\sigma}(R) = \langle \Phi | \hat{c}^\dagger_{R,b,\sigma} \hat{c}_{R,b',\sigma} | \Phi \rangle \) and the Gutzwiller variational parameters \( \lambda_{\Gamma,\Gamma'}(R) \). For example,

\[
V^G_{\text{loc}} = \sum_{R} \sum_{\Gamma,\Gamma'} \lambda_{R;\Gamma} E^{\text{loc}}_{R;\Gamma,\Gamma'} \langle \hat{m}_{R;\Gamma,\Gamma'} \rangle_{\Phi} \lambda_{R;\Gamma'}.
\] (59)
For $\mathbf{R} \neq \mathbf{R}'$, the correlated single-particle density matrix becomes

$$\rho_{(\mathbf{R}',\mathbf{b}'),(\mathbf{R},\mathbf{b})}\sigma = \sum_{a,a'} q_{a,\sigma}(\mathbf{R}) \left( q_{a',\sigma}(\mathbf{R}') \right)^* \rho_{(\mathbf{R}',a'),(\mathbf{R},a);\sigma} \cdot (60)$$

The orbital-dependent factors $q_{a,\sigma}(\mathbf{R})$ reduce the band width of the correlated orbitals and their hybridizations with other orbitals.

**Results**

- In the limit $Z \to \infty$, the Gutzwiller many-body problem is solved without further approximations.
- ‘Solve the Gutzwiller–Kohn-Sham equations’ ⊕ ‘Minimize with respect to the Gutzwiller parameters $\lambda_{\mathbf{R};\Gamma}$’ is similar in complexity to the DFT. For simple systems such as nickel and iron, the latter minimization is computationally inexpensive ($\lesssim 50\%$ of total CPU time).
Transition metals

For translational invariant lattice systems, the quasi-particle (`Gutzwiller–Kohn-Sham`) Hamiltonian becomes

\[
\hat{H}_{\text{qp}}^G = \sum_{\mathbf{k}, b, b', \sigma} h_{b, b'; \sigma}^G(\mathbf{k}) \hat{c}_{\mathbf{k}, b, \sigma}^\dagger \hat{c}_{\mathbf{k}, b', \sigma}
\]  

(61)

with the matrix elements in the orbital Bloch basis

\[
h_{b, b'; \sigma}^G(\mathbf{k}) = \eta_{b, b'; \sigma} + \sum_{a, a'} q_{a, \sigma}^{b, \sigma} (q_{a', \sigma}^{b', \sigma})^* h_{a, a'; \sigma}^0(\mathbf{k}),
\]

(62)

\[
h_{a, a'; \sigma}^0(\mathbf{k}) = \int d\mathbf{r} \phi_k^{*, a, \sigma}(\mathbf{r}) \left(-\frac{\Delta r}{2m} + V_{\sigma}^H(\mathbf{r})\right) \phi_{k', a', \sigma}(\mathbf{r}),
\]

\[
V_{\sigma}^H(\mathbf{r}) = U(\mathbf{r}) + V_{\text{Har}}(\mathbf{r}) + v_{\text{H,xc}, \sigma}(\mathbf{r}).
\]

\(\eta_{b, b'; \sigma}\): Lagrange parameters (variational band-shifts).
In cubic symmetry, the local interaction for $3d$ electrons reads

$$\hat{V}_{\text{full}} = \hat{V}_{\text{loc}}^{\text{dens}} + \hat{V}_{\text{loc}}^{\text{sf}} + \hat{V}_{\text{loc}}^{(3)} + \hat{V}_{\text{loc}}^{(4)},$$

$$\hat{V}_{\text{loc}}^{\text{dens}} = \sum_{c,\sigma} U(c, c) \hat{n}_{c,\sigma} \hat{n}_{c,\bar{\sigma}} + \sum_{c(\neq)c'} \sum_{\sigma,\sigma'} \tilde{U}_{\sigma,\sigma'}(c, c') \hat{n}_{c,\sigma} \hat{n}_{c',\sigma'},$$

$$\hat{V}_{\text{loc}}^{\text{sf}} = \sum_{c(\neq)c'} J(c, c') \left( \hat{c}_{c,\uparrow} \hat{c}_{c,\downarrow} \hat{c}_{c',\bar{\downarrow}} \hat{c}_{c',\bar{\uparrow}} + \text{h.c.} \right)$$

$$+ \sum_{c(\neq)c';\sigma} J(c, c') \hat{c}_{c,\sigma} \hat{c}_{c',\bar{\sigma}} \hat{c}_{c,\bar{\sigma}} \hat{c}_{c',\sigma}. \quad (63)$$

Here, $\uparrow = \downarrow (\downarrow = \uparrow)$ and $\tilde{U}_{\sigma,\sigma'}(c, c') = U(c, c) - \delta_{\sigma,\sigma'} J(c, c').$

$U \equiv U(c, c)/2$ and $J \equiv J(c, c')$ are local Hubbard and Hund’s-rule exchange interactions. DMFT calculations often employ $\hat{V}_{\text{loc}}^{\text{dens}}$ only (reduction of the numerical effort).
Gutzwiller calculations include the full $\hat{V}_{\text{loc}}$ with the spin-flip terms and the three-orbital and four-orbital terms

$$\hat{V}_{\text{loc}}^{(3)} = \sum_{t;\sigma,\sigma'} \left( T(t) - \delta_{\sigma,\sigma'} A(t) \right) \hat{n}_{t,\sigma} \hat{c}_{u,\sigma'}^\dagger \hat{c}_{v,\sigma} + \text{h.c.} \right), \quad (64)$$

$$+ \sum_t A(t) \left( \hat{c}_{t,\sigma}^\dagger \hat{c}_{t,\sigma'}^\dagger \hat{c}_{u,\sigma} \hat{c}_{v,\sigma} + \hat{c}_{t,\sigma}^\dagger \hat{c}_{u,\sigma'}^\dagger \hat{c}_{t,\sigma'} \hat{c}_{v,\sigma} + \text{h.c.} \right)$$

$$\hat{V}_{\text{loc}}^{(4)} = \sum_{t(\neq) t'(\neq) t''} \sum_{\sigma,\sigma'} S(t, t'; t'', e) \hat{c}_{t,\sigma}^\dagger \hat{c}_{t',\sigma'}^\dagger \hat{c}_{t'',\sigma'} \hat{c}_{e,\sigma} + \text{h.c.}$$

Here, $t = \zeta, \eta, \xi$ ($t_{2g}$ orbitals) with symmetries $\zeta = xy$, $\eta = xz$, and $\xi = yz$, and $e = u, v$ (two $e_g$ orbitals) with symmetries $u = 3z^2 - r^2$ and $v = x^2 - y^2$. 
There exists no systematic (let alone rigorous) derivation of the double-counting corrections.

In the context of the LDA+\(U\) method, it was suggested to use

\[
V_{\text{dc}}^{\text{LDA}+U} = \frac{U}{2} \bar{n}(\bar{n} - 1) - \frac{J}{2} \sum_{\sigma} \bar{n}_{\sigma}(1 - \bar{n}_{\sigma}),
\]

(65)

where \(\bar{n}_{\sigma}\) is the sum of \(\sigma\)-electrons in the correlated orbitals. In effect, the double-counting corrections generate a band shift

\[
\eta^{\text{dc}}_{c,c;\sigma} = -\left[ U \left( \bar{n} - 1/2 \right) + J \left( \bar{n}_{\sigma} - 1/2 \right) \right].
\]

(66)

It guarantees that the Hubbard interaction does not empty the 3d-levels.
Transition metals

Problems

- The choice of the double-counting correction is guess-work.
- The double-counting corrections have no orbital resolution.
- The double-counting corrections do not work, e.g., for Cerium.

There is the big risk that the physics is determined by the choice of the double-counting corrections!

Double counting corrections for iron and nickel

Nickel: The 3$d$-shell is almost filled, $n_{3d} \approx 9/10$. Here, the form of the double-counting corrections is not decisive for the ground-state properties.

Iron: standard double-counting corrections still work satisfactorily.
Further simplifications for iron and nickel

- Assume identical radial parts for the $t_{2g}$ and $e_g$ orbitals (‘spherical approximation’). Then, three Racah parameters $A, B, C$ determine all Coulomb parameters, e.g., $U = A + 4B + 3C, J = 5B/2 + C$.

- Use $C/B = 4$, as is appropriate for neutral atoms. Then, $U$ and $J$ determine the atomic spectrum completely.

- In cubic symmetry, some matrices become diagonal

\[ q_{c',\sigma}^c = \delta_{c,c'} \left( \delta_{c,t_{2g},\sigma} q_{t,\sigma} + \delta_{c,e_g,\sigma} q_{e,\sigma} \right), \quad (67) \]

\[ \rho_{G,(R,b'),(R,b);\sigma}^G = \delta_{b,b'} \rho_{(R,b),(R,b);\sigma}. \quad (68) \]

Then, we recover expressions used in previous phenomenological treatments of the Gutzwiller-DFT.
Transition metals

Implementation

- We use QuantumEspresso as DFT code (open source, based on plane waves, employs ultra-soft pseudo-potentials).
- ‘Poor-man’ Wannier orbitals for 3d electrons.

Hubbard parameters

The ‘best values’ for $U$ and $J$ depend on

- the quality of the correlated orbitals; better localized orbitals require larger Coulomb interactions;
- the accuracy of the local interaction; using only density-density interactions requires smaller Coulomb parameters;
- The choice of the double-counting corrections.
Transition metals

We fix $U$ and $J$ for Ni from a comparison of the lattice constant and the spin-only magnetic moment.

In DFT: the lattice constant is too small; the Gutzwiller approach resolves this problem when we choose $U > 10 \text{ eV}$.

Fig. 2: Fcc lattice constant of nickel as a function of $U$ for different values of $J/U$, calculated with the full local Hamiltonian $\hat{V}_{\text{loc}}^{\text{full}}$ and the LDA+$U$ double counting correction; dashed line: experimental value.
In order to fix both $U$ and $J$, we must also consider the spin-only magnetic moment.

![Graph showing magnetic moment as a function of $U$ for different values of $J/U$.](image)

**Fig. 3:** Magnetic moment of nickel as a function of $U$ for different values of $J/U$, calculated with the full local Hamiltonian $\hat{V}_{\text{loc}}^\text{full}$ and the LDA+$U$ double counting correction; dashed line: experimental value.

When we choose $U_{\text{opt}} = 13 \text{ eV}$ and $J_{\text{opt}} = 0.9 \text{ eV}$ ($J/U = 0.07$), we obtain a good agreement with the experimental values for $a$ and $m$. 
Transition metals

For $U_{\text{opt}} = 13 \text{ eV}$ and $J_{\text{opt}} = 0.9 \text{ eV}$ ($J/U = 0.07$), we calculate the bulk modulus.

Fig. 4: Ground-state energy per particle $E_0(a)/N$ relative to its value at $a = 6.63a_B$ as a function of the fcc lattice parameter $a/a_B$, calculated with the full local Hamiltonian $\hat{V}_{\text{loc}}^{\text{full}}$ and the LDA+$U$ double counting correction; full line: 2nd-order polynomial fit.

$K_G = 169 \text{ GPa}$, in good agreement with experiment, $K = 182 \text{ GPa}$, whereas $K_{\text{DFT}} = 245 \text{ GPa}$. 
Transition metals

For $U_{\text{opt}} = 13\,\text{eV}$ and $J_{\text{opt}} = 0.9\,\text{eV}$ ($J/U = 0.07$), we derive the quasi-particle band structure.

Fig. 5: Landau-Gutzwiller quasi-particle band structure of fcc nickel along high-symmetry lines in the first Brillouin zone, calculated with the full local Hamiltonian and the LDA+$U$ double-counting correction; left: majority spin; right: minority spin. Fermi energy $E_{\text{F}}^G = 0$. 
Transition metals

<table>
<thead>
<tr>
<th>Symmetry</th>
<th>Experiment</th>
<th>$\hat{V}<em>{\text{full}}</em>{\text{loc}}$</th>
<th>$\hat{V}<em>{\text{dens}}</em>{\text{loc}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\langle \Gamma_1 \rangle$</td>
<td>$8.90 \pm 0.30$</td>
<td>$8.95[0.08]$</td>
<td>$8.93[0.08]$</td>
</tr>
<tr>
<td>$\langle X_1 \rangle$</td>
<td>$3.30 \pm 0.20$</td>
<td>$3.37[0.27]$</td>
<td>$3.42[0.10]$</td>
</tr>
<tr>
<td>$X_{2\uparrow}$</td>
<td>$0.21 \pm 0.03$</td>
<td>$0.26$</td>
<td>$0.13$</td>
</tr>
<tr>
<td>$X_{2\downarrow}$</td>
<td>$0.04 \pm 0.03$</td>
<td>$0.14$</td>
<td>$0.21$</td>
</tr>
<tr>
<td>$X_{5\uparrow}$</td>
<td>$0.15 \pm 0.03$</td>
<td>$0.32$</td>
<td>$0.41$</td>
</tr>
<tr>
<td>$\Delta_{e_g}(X_2)$</td>
<td>$0.17 \pm 0.05$</td>
<td>$0.12$</td>
<td>$-0.08$</td>
</tr>
<tr>
<td>$\Delta_{t_{2g}}(X_5)$</td>
<td>$0.33 \pm 0.04$</td>
<td>$0.60$</td>
<td>$0.70$</td>
</tr>
<tr>
<td>$\langle L_{2'} \rangle$</td>
<td>$1.00 \pm 0.20$</td>
<td>$0.14[0.06]$</td>
<td>$0.12[0.06]$</td>
</tr>
<tr>
<td>$\langle \Lambda_{3;1/2} \rangle$</td>
<td>$0.50[0.21 \pm 0.02]$</td>
<td>$0.64[0.30]$</td>
<td>$0.60[0.16]$</td>
</tr>
</tbody>
</table>

Quasi-particle band energies with respect to the Fermi energy in eV at various high-symmetry points (counted positive for occupied states). $\langle \ldots \rangle$ indicates the spin average, errors bars in the experiments without spin resolution are given as $\pm$. Theoretical data show the spin average and the exchange splittings in square brackets.
Transition metals

Improvements

- Gutzwiller-DFT gets the correct 3d bandwidth ($W_{G\text{-DFT}} = 3.3 \text{ eV}$, whereas $W_{\text{DFT}} = 4.5 \text{ eV}$).
- Gutzwiller-DFT gets the correct Fermi-surface topology (only one hole ellipsoid at the X-point).
- The positions of the bands are OK, by and large.
- The band at $L_2'$ are pure 3p-like (not correlated – yet!).
- The full local interaction gives somewhat better results than the density-only interaction.

Refinements are to be expected when we improve the description (orbital-dependent double counting, spin-orbit coupling).
Transition metals

We fix $U$ and $J$ for Fe from a comparison of the lattice constant and the spin-only magnetic moment.

![Graph showing the Bcc lattice constant of iron as a function of $U$ for different values of $J/U$, calculated with the full local Hamiltonian $\hat{V}_{\text{loc}}^\text{full}$ and the LDA+$U$ double counting correction; dashed line: experimental value.]

In DFT: the lattice constant is too small; the Gutzwiller approach resolves this problem when we choose $U > 8 \text{ eV}$. 

Fig. 6: Bcc lattice constant of iron as a function of $U$ for different values of $J/U$, calculated with the full local Hamiltonian $\hat{V}_{\text{loc}}^\text{full}$ and the LDA+$U$ double counting correction; dashed line: experimental value.
In order to fix both $U$ and $J$, we must also consider the spin-only magnetic moment.

When we choose $U_{\text{opt}} = 9 \text{ eV}$ and $J_{\text{opt}} = 0.54 \text{ eV}$ ($J/U = 0.06$), we obtain a good agreement with the experimental values for $a$ and $m$.

Fig. 7: Magnetic moment of iron as a function of $U$ for different values of $J/U$, calculated with the full local Hamiltonian $\hat{V}_{\text{loc}}^{\text{full}}$ and the LDA$+U$ double counting correction; dashed line: experimental value.
Transition metals

For $U_{\text{opt}} = 9 \text{ eV}$ and $J_{\text{opt}} = 0.54 \text{ eV}$ ($J/U = 0.06$), we calculate the bulk modulus.

Fig. 8: Energy per atom $e(v)$ in units of eV as a function of the unit-cell volume $v$ in units of $a_B^3$ for non-magnetic and ferromagnetic bcc iron and non-magnetic hcp iron at $U = 9 \text{ eV}$ and $J = 0.54 \text{ eV}$ and ambient pressure. The energies are shifted by the same value.

$K_G = 165 \text{ GPa}$, in good agreement with $K_{\text{exp}} = 170 \text{ GPa}$ from experiment, whereas $K_{\text{LDA}} = 227 \text{ GPa}$ and $K_{\text{GGA}} = 190 \text{ GPa}$.
Transition metals

For $U_{\text{opt}} = 9 \, \text{eV}$ and $J_{\text{opt}} = 0.54 \, \text{eV}$ ($J/U = 0.06$), we derive the quasi-particle band structure.

Fig. 9: Landau-Gutzwiller quasi-particle band structure (full lines) and DFT(LDA) bands (dashed lines) of bcc iron (left) and hcp iron (right) along high-symmetry lines in the first Brillouin zone, calculated with the full local Hamiltonian and the LDA+$U$ double-counting correction; Fermi energy $E_F^G = 0$. 
Transition metals

Improvements and remaining issues

- The electronic correlations guarantee the correct ground-state structure (ferromagnetic bcc iron) even when the LDA exchange-correlation potential is used. It is not necessary to resort to gradient corrections (GGA).

- Gutzwiller-DFT improves the $3d$ bandwidth. The bandwidth reduction is not as large as in nickel.

- The effective mass enhancement at the Fermi energy cannot be explained satisfactorily within the Gutzwiller approach. Large ratios, $m^*/m \gtrsim 3$ in some directions, must be due to the coupling to magnons.

- The spin-orbit coupling is considered only phenomenologically.
Summary of part II

What have you learned?

- **Formalism:**
  - A formal derivation of the Gutzwiller Density Functional Theory is given.
  - Explicit expressions for all required expectation values are available in the limit of large lattice coordination number.
  - For simple cases such as nickel, previous ad-hoc formulations of G-DFT are proven to be correct.

- **Results for nickel and iron:**
  - Experimental values for the lattice constant, the bulk modulus and the magnetic moment are reproduced for $(U = 13 \text{ eV}, J = 0.9 \text{ eV})_{\text{Ni}}$ and $(U = 9 \text{ eV}, J = 0.54 \text{ eV})_{\text{Fe}}$.
  - The experimental crystal structure, bandwidth, Fermi surface topology, and overall band structure are reproduced fairly well.
  - No fine tuning of parameters is required.
Summary of part II

Outlook

- The Gutzwiller DFT is a generic extension of the DFT framework; however, it is not fully ‘ab initio’!
- It is a numerically affordable method to include correlations.
- Our present implementation is based on the limit of infinite lattice coordination number.

Open problems

- The spin-orbit coupling must be implemented.
- The method must be applied to other materials.
- The double-counting problem must be solved in a canonical way; ad-hoc potentials are not helpful in the long run.
Thank you for your attention!