Gutzwiller Density Functional Theory

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The many-body problem in solid-state theory

(see talk by R. Martin)

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

$$\begin{aligned} \hat{H} &= \hat{H}_{\text{band}} + \hat{H}_{\text{int}} \ , \\ \hat{H}_{\text{band}} &= \sum_{\sigma} \int \mathrm{d}\mathbf{r} \hat{\psi}^{\dagger}_{\sigma}(\mathbf{r}) \left(-\frac{\Delta_{\mathbf{r}}}{2m} + U(\mathbf{r}) \right) \hat{\psi}_{\sigma}(\mathbf{r}) \ , \qquad (1) \\ \hat{H}_{\text{int}} &= \sum_{\sigma,\sigma'} \int \mathrm{d}\mathbf{r} \int \mathrm{d}\mathbf{r}' \hat{\psi}^{\dagger}_{\sigma}(\mathbf{r}) \hat{\psi}^{\dagger}_{\sigma'}(\mathbf{r}') V(\mathbf{r}-\mathbf{r}') \hat{\psi}_{\sigma'}(\mathbf{r}') \hat{\psi}_{\sigma}(\mathbf{r}) \ . \end{aligned}$$

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

$$V(\mathbf{r}-\mathbf{r}') = \frac{1}{2} \frac{e^2}{|\mathbf{r}-\mathbf{r}'|} \ , \ U(\mathbf{r}) = \sum_{\mathbf{R}} \frac{e^2}{|\mathbf{r}-\mathbf{R}|} \qquad (2)$$

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

Outline of Part II

Part I

Gutzwiller variational approach

Hubbard model: a toy model for interacting electrons

(see talk by R. Eder)

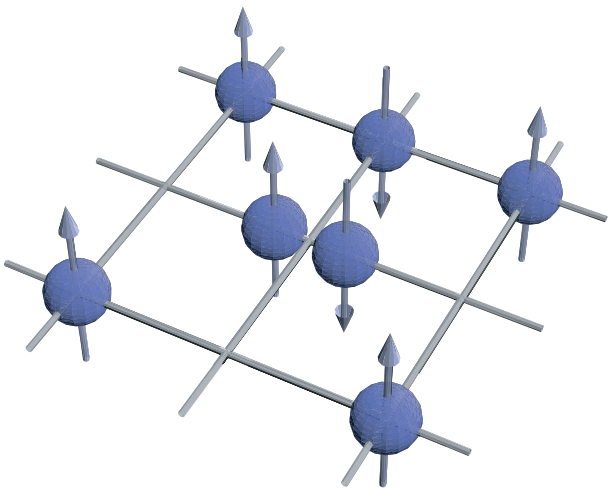

Fig. 1: Electrons with spin $\sigma = \uparrow, \downarrow$ on a lattice

Kinetic term

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

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

Hubbard interaction

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

U: strength of the Coulomb repulsion

Single-band Hubbard Hamiltonian

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

Hubbard model: a toy model for interacting electrons

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)

$$\begin{aligned}\hat{H} &= \sum_{\mathbf{R},\mathbf{R}';\sigma} t^{b}_{\mathbf{R}-\mathbf{R}'}\, \hat{c}^{+}_{\mathbf{R},b,\sigma}\, \hat{c}_{\mathbf{R}',b,\sigma} \\ &\quad + \sum_{\mathbf{R}} \sum_{\substack{b_1,\ldots,b_4;\\ \sigma_1,\ldots\sigma_4}} U^{b_3\sigma_3,b_4\sigma_4}_{b_1\sigma_1,b_2\sigma_2}\, \hat{c}^{+}_{\mathbf{R},b_1,\sigma_1}\, \hat{c}^{+}_{\mathbf{R},b_2,\sigma_2}\, \hat{c}_{\mathbf{R},b_3,\sigma_3}\, \hat{c}_{\mathbf{R},b_4,\sigma_4} \qquad (6)\end{aligned}$$

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

$$|\Psi_{\mathrm{G}}\rangle = \hat{P}_{\mathrm{G}}|\Phi\rangle \ , \ \hat{P}_{\mathrm{G}} = g^{\hat{D}} \ , \tag{7}$$

where

$\lvert\Psi_{\mathrm{G}}\rangle$	:	Gutzwiller variational state
$\lvert\Phi\rangle$	:	single-particle product state, e.g., the Fermi sea
$\hat{P}_{\mathrm{G}}$	:	Gutzwiller correlator
g	:	real variational parameter
$\hat{D}$	$=$	$\sum_{\mathbf{R}} \hat{n}_{\mathbf{R},\uparrow}\hat{n}_{\mathbf{R},\downarrow}$: 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 $t^{b}_{\mathbf{R}-\mathbf{R}'} \equiv 0$, we must work with the atomic eigenstates $|\Gamma\rangle$ of $\hat{V}$,

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

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

Gutzwiller Ansatz for the multi-band Hubbard model

$$|\Psi_{\mathrm{G}}\rangle = \hat{P}_{\mathrm{G}}|\Phi\rangle \quad , \quad \hat{P}_{\mathrm{G}} = \prod_{\mathbf{R}} \prod_{\Gamma_{\mathbf{R}}} \lambda^{\hat{m}_{\mathbf{R};\Gamma}}_{\mathbf{R};\Gamma} = \prod_{\mathbf{R}} \sum_{\Gamma_{\mathbf{R}}} \lambda_{\mathbf{R};\Gamma}\, \hat{m}_{\mathbf{R};\Gamma} \ , \quad (9)$$

where

$|\Psi_{\mathrm{G}}\rangle$: Gutzwiller variational state

$\lambda_{\mathbf{R};\Gamma}$: 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

$$|\Psi_0\rangle \sim \big(|\uparrow_1,\downarrow_2\rangle - |\downarrow_1,\uparrow_2\rangle\big) + \alpha(U/t)\big(|\uparrow\downarrow_1,\emptyset_2\rangle + |\emptyset_1,\uparrow\downarrow_2\rangle\big) \quad (10)$$

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

$$|\Psi_\mathrm{G}\rangle \sim \big(|\uparrow_1,\downarrow_2\rangle - |\downarrow_1,\uparrow_2\rangle\big) + g\big(|\uparrow\downarrow_1,\emptyset_2\rangle + |\emptyset_1,\uparrow\downarrow_2\rangle\big) \quad (11)$$

Ritz's variational principle thus gives $g^\mathrm{opt} = \alpha(U/t)$: 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

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

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

$$t \sim t^*/\sqrt{Z}\,. \tag{13}$$

Evaluation in high dimensions

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

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

Collapse of diagrams in position space

When two inner vertices $\mathbf{f}_1$ and $\mathbf{f}_2$ are connected by three different paths, we may set $\mathbf{f}_1 = \mathbf{f}_2$ in the limit $Z \to \infty$ because the summation over $Z^{||\mathbf{f}_1-\mathbf{f}_2||}$ neighbors cannot compensate the factor $Z^{-3||\mathbf{f}_1-\mathbf{f}_2||/2}$ from the three lines for $\mathbf{f}_1 \neq \mathbf{f}_2$.

How can we get rid of the remaining local contributions?

Evaluation in high dimensions

Diagrammatic expansion for Gutzwiller states

1. Develop a diagrammatic perturbation theory with vertices $x_{\mathbf{f},l_1,l_2}$ and lines $\widetilde{P}^0_\sigma(\mathbf{f}_1, b_1; \mathbf{f}_2, b_2)$;
2. Choose the expansion parameters $x_{\mathbf{f},l_1,l_2}$ 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,

$$\widetilde{P}^0_\sigma(\mathbf{f}, b; \mathbf{f}, b') = 0 \; ; \tag{15}$$

3. In the limit $Z \to \infty$, 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.

Evaluation in high dimensions

We use the representation ($\hat{P}_{\mathrm{G}} = \prod_{\mathbf{f}} \hat{P}_{\mathrm{G},\mathbf{f}}$)

$$\hat{P}^2_{\mathrm{G},\mathbf{f}} = 1 + x_{\mathbf{f}}(\hat{n}_{\mathbf{f},\uparrow} - \langle \hat{n}_{\mathbf{f},\uparrow} \rangle_{\Phi})(\hat{n}_{\mathbf{f},\downarrow} - \langle \hat{n}_{\mathbf{f},\downarrow} \rangle_{\Phi}) \; . \tag{16}$$

Note: the Hartree contributions are eliminated by construction, there are only inner vertices vertices with four lines.
Now that we also have ($\hat{P}_{\mathrm{G},\mathbf{f}} = \sum_{\Gamma} \lambda_{\mathbf{f};\Gamma} \hat{m}_{\mathbf{f};\Gamma}$)

$$\begin{aligned} \hat{P}^2_{\mathrm{G},\mathbf{f}} \;\; = \;\; & \lambda^2_{\mathbf{f};\emptyset}(1 - \hat{n}_{\mathbf{f},\uparrow})(1 - \hat{n}_{\mathbf{f},\downarrow}) + \lambda_{\mathbf{f};\uparrow\downarrow} \hat{n}_{\mathbf{f},\uparrow} \hat{n}_{\mathbf{f},\downarrow} \\ & + \lambda^2_{\mathbf{f};\uparrow} \hat{n}_{\mathbf{f},\uparrow}(1 - \hat{n}_{\mathbf{f},\downarrow}) + \lambda^2_{\mathbf{f};\downarrow}(1 - \hat{n}_{\mathbf{f},\uparrow}) \hat{n}_{\mathbf{f},\downarrow} \; , \end{aligned} \tag{17}$$

so that we know $\lambda_{\mathbf{f};\emptyset}$, $\lambda_{\mathbf{f};\sigma}$ and $\lambda_{\mathbf{f};\uparrow\downarrow}$ as a function of $x_{\mathbf{f}}$.
In infinite dimensions ($\mathbf{R} \neq \mathbf{R}'$)

$$\begin{aligned} \langle \hat{n}_{\mathbf{R};\uparrow} \hat{n}_{\mathbf{R};\downarrow} \rangle_{\mathrm{G}} \;\; &= \;\; \lambda^2_{\mathbf{R};\uparrow\downarrow} \langle \hat{n}_{\mathbf{R},\uparrow} \rangle_{\Phi} \langle \hat{n}_{\mathbf{R},\downarrow} \rangle_{\Phi} \; , \\ \langle \hat{c}^{+}_{\mathbf{R},\sigma} \hat{c}_{\mathbf{R}',\sigma} \rangle_{\mathrm{G}} \;\; &= \;\; q_{\mathbf{R},\sigma} q_{\mathbf{R}',\sigma} \langle \hat{c}^{+}_{\mathbf{R},\sigma} \hat{c}_{\mathbf{R}',\sigma} \rangle_{\Phi} \; . \end{aligned} \tag{18}$$

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

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

$$E_{\mathrm{var}} = \langle \Phi | \hat{H}_0^{\mathrm{eff}} | \Phi \rangle + UL\lambda_{\uparrow\downarrow}^2 \ , \ \hat{H}_0^{\mathrm{eff}} = \sum_{\mathbf{k}} \left[q^2 \epsilon(\mathbf{k}) \right] \hat{n}_{\mathbf{k};\sigma} \qquad (19)$$

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

$$\langle \hat{D}/L \rangle_{\mathrm{G}} = \frac{\lambda_{\uparrow\downarrow}^2}{4} = \frac{1}{4}\left(1 - \frac{U}{U_{\mathrm{BR}}}\right) \ , \ q^2 = 1 - \left(\frac{U}{U_{\mathrm{BR}}}\right)^2 \ . \qquad (20)$$

All particles are localized beyond $U_{\mathrm{BR}} = 8|\langle \hat{T} \rangle_0 / L|$ (BR insulator).

Evaluation in high dimensions

Quasi-particle picture

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

- Landau's idea of quasi-particles
  Fermi gas + hole exc. $\overset{\text{interactions}}{\longrightarrow}$ Fermi liquid + quasi-hole exc.
- Realization in terms of Gutzwiller wave functions
  Fermi-gas ground state: $|\Phi\rangle = \prod_{\mathbf{p},\sigma;\epsilon(\mathbf{p})\leq E_{\mathrm{F}}} \hat{h}^{+}_{\mathbf{p},\sigma}|\mathrm{vac}\rangle$
  Fermi-liquid ground state: $|\Psi_{\mathrm{G}}\rangle = \hat{P}_{\mathrm{G}}|\Phi\rangle$
  hole excitation: $\hat{h}_{\mathbf{p},\sigma}|\Phi\rangle$
  quasi-hole excitation: $|\Psi_{\mathrm{G};\mathbf{p},\sigma}\rangle = \hat{P}_{\mathrm{G}}\hat{h}_{\mathbf{p},\sigma}|\Phi\rangle$
- Energy of Landau-Gutzwiller quasi-particles

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

$\widetilde{\epsilon}_{\sigma}(\mathbf{p})$: dispersion relation of $\hat{H}_0^{\mathrm{eff}}$; here: $\widetilde{\epsilon}_{\sigma}(\mathbf{p}) = q^2\epsilon(\mathbf{p})$.

Summary of part I

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 ($\sigma = \uparrow, \downarrow$; $\hbar \equiv 1$)

$$\begin{aligned} \hat{H} &= \hat{H}_{\text{band}} + \hat{H}_{\text{int}} \,, \\ \hat{H}_{\text{band}} &= \sum_{\sigma} \int \mathrm{d}\mathbf{r} \hat{\psi}^{\dagger}_{\sigma}(\mathbf{r}) \left(-\frac{\Delta_{\mathbf{r}}}{2m} + U(\mathbf{r}) \right) \hat{\psi}_{\sigma}(\mathbf{r}) \,, \qquad (22) \\ \hat{H}_{\text{int}} &= \sum_{\sigma,\sigma'} \int \mathrm{d}\mathbf{r} \int \mathrm{d}\mathbf{r}' \hat{\psi}^{\dagger}_{\sigma}(\mathbf{r}) \hat{\psi}^{\dagger}_{\sigma'}(\mathbf{r}') V(\mathbf{r}-\mathbf{r}') \hat{\psi}_{\sigma'}(\mathbf{r}') \hat{\psi}_{\sigma}(\mathbf{r}) \,. \end{aligned}$$

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

$$V(\mathbf{r}-\mathbf{r}') = \frac{1}{2} \frac{e^2}{|\mathbf{r}-\mathbf{r}'|} \,, \quad U(\mathbf{r}) = \sum_{\mathbf{R}} \frac{e^2}{|\mathbf{r}-\mathbf{R}|} \qquad (23)$$

Density Functional Theory

Ritz variational principle

Task: minimize the energy functional

$$E\left[\{|\Psi\rangle\}\right] = \frac{\langle\Psi|\hat{H}|\Psi\rangle}{\langle\Psi|\Psi\rangle} . \tag{24}$$

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!

Density Functional Theory

Consider all normalized states $|\Psi^{(n)}\rangle$ for given 'physical' densities

$$n_\sigma(\mathbf{r}) = \langle\Psi^{(n)}|\hat{\Psi}^\dagger_\sigma(\mathbf{r})\hat{\Psi}_\sigma(\mathbf{r})|\Psi^{(n)}\rangle \ . \tag{25}$$

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

$$\begin{aligned}
\hat{H}_\mathrm{kin} &= \sum_\sigma \int \mathrm{d}\mathbf{r}\hat{\Psi}^\dagger_\sigma(\mathbf{r}) \left(-\frac{\Delta_\mathbf{r}}{2m}\right) \hat{\Psi}_\sigma(\mathbf{r}) \ , \qquad (26)\\
\hat{V}_\mathrm{xc} &= \sum_{\sigma,\sigma'} \int \mathrm{d}\mathbf{r} \int \mathrm{d}\mathbf{r}' V(\mathbf{r}-\mathbf{r}') \Big[\hat{\Psi}^\dagger_\sigma(\mathbf{r})\hat{\Psi}^\dagger_{\sigma'}(\mathbf{r}')\hat{\Psi}_{\sigma'}(\mathbf{r}')\hat{\Psi}_\sigma(\mathbf{r}) \\
&\qquad - 2\hat{\Psi}^\dagger_\sigma(\mathbf{r})\hat{\Psi}_\sigma(\mathbf{r})n_{\sigma'}(\mathbf{r}') + n_\sigma(\mathbf{r})n_{\sigma'}(\mathbf{r}')\Big] \ .
\end{aligned}$$

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

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

for fixed densities $n_\sigma(\mathbf{r})$. 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,

$$\text{Kinetic:} \quad K\left[\{n_\sigma(\mathbf{r})\}\right] = \langle\Psi_0^{(n)}|\hat{H}_{\rm kin}|\Psi_0^{(n)}\rangle \,, \quad (28)$$

$$\text{Exchange-correlation:} \quad E_{\rm xc}\left[\{n_\sigma(\mathbf{r})\}\right] = \langle\Psi_0^{(n)}|\hat{V}_{\rm xc}|\Psi_0^{(n)}\rangle \,. \quad (29)$$

Density Functional Theory

Density Functional

Task: minimize the Density Functional

$$\begin{aligned} D\left[\{n_\sigma(\mathbf{r})\}\right] &= K\left[\{n_\sigma(\mathbf{r})\}\right] + E_{\mathrm{xc}}\left[\{n_\sigma(\mathbf{r})\}\right] \\ &\quad + U\left[\{n_\sigma(\mathbf{r})\}\right] + V_{\mathrm{Har}}\left[\{n_\sigma(\mathbf{r})\}\right] \end{aligned} \tag{30}$$

with the ionic/Hartree energies

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

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

The minimization provides the ground-state densities $n^0_\sigma(\mathbf{r})$ and the ground-state energy $E_0 = D\left[\{n^0_\sigma(\mathbf{r})\}\right]$.

Density Functional Theory

Problem

The minimization of the energy functional in eq. (27) poses an **extremely difficult** many-particle problem. Thus, the exact density functional $D[\{n_\sigma(\mathbf{r})\}]$ 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

$$n_\sigma^{\rm sp}(\mathbf{r}) = \langle \Phi^{(n)} | \hat{\Psi}_\sigma^\dagger(\mathbf{r}) \hat{\Psi}_\sigma(\mathbf{r}) | \Phi^{(n)} \rangle \; . \tag{32}$$

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

$$F_{\rm sp}\left[\{n_\sigma^{\rm sp}(\mathbf{r})\}, \left\{|\Phi^{(n)}\rangle\right\}\right] = \langle \Phi^{(n)} | \hat{H}_{\rm kin} | \Phi^{(n)} \rangle \; . \tag{33}$$

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

$$K_{\rm sp}\left[\{n_\sigma^{\rm sp}(\mathbf{r})\}\right] = \langle \Phi_0^{(n)} | \hat{H}_{\rm kin} | \Phi_0^{(n)} \rangle \; . \tag{34}$$

Density Functional Theory

The single-particle density functional is *defined* as

$$\begin{aligned} D_{\mathrm{sp}}\left[\{n_\sigma^{\mathrm{sp}}(\mathbf{r})\}\right] &= K_{\mathrm{sp}}\left[\{n_\sigma^{\mathrm{sp}}(\mathbf{r})\}\right] + U\left[\{n_\sigma^{\mathrm{sp}}(\mathbf{r})\}\right] + V_{\mathrm{Har}}\left[\{n_\sigma^{\mathrm{sp}}(\mathbf{r})\}\right] \\ &\quad + E_{\mathrm{sp,xc}}\left[\{n_\sigma^{\mathrm{sp}}(\mathbf{r})\}\right] \end{aligned} \tag{35}$$

with the yet unspecified single-particle exchange-correlation energy $E_{\mathrm{sp,xc}}\left[\{n_\sigma^{\mathrm{sp}}(\mathbf{r})\}\right]$.

Assumption: non-interacting V-representability

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

$$n_\sigma^{\mathrm{sp}}(\mathbf{r}) = n_\sigma(\mathbf{r})\ . \tag{36}$$

Density Functional Theory

Hohenberg-Kohn theorem

We demand

$$D_{\mathrm{sp}}\left[\{n_\sigma(\mathbf{r})\}\right] = D\left[\{n_\sigma(\mathbf{r})\}\right]. \tag{37}$$

$\Rightarrow$ The single-particle substitute system has the same ground-state density $n_\sigma^0(\mathbf{r})$ and energy E_0 as the many-particle Hamiltonian.

Single-particle exchange-correlation energy

To fulfill eq. (37), we *define*

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

Problem

We know neither of the quantities on the r.h.s. of eq. (38)!

Density Functional Theory

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

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

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

$$\hat{\Psi}^\dagger_\sigma(\mathbf{r}) = \sum_n \psi^*_n(\mathbf{r})\hat{b}^\dagger_{n,\sigma} \quad , \quad \hat{\Psi}_\sigma(\mathbf{r}) = \sum_n \psi_n(\mathbf{r})\hat{b}_{n,\sigma} . \quad (40)$$

Density Functional Theory

With the Hartree and exchange-correlation potentials

$$\begin{aligned} V_{\mathrm{Har}}(\mathbf{r}) &\equiv \sum_{\sigma'} \int \mathrm{d}\mathbf{r}' 2V(\mathbf{r}-\mathbf{r}')n^0_{\sigma'}(\mathbf{r}') \,, \\ v_{\mathrm{sp,xc},\sigma}(\mathbf{r}) &\equiv \left. \frac{\partial E_{\mathrm{sp,xc}}\left[\{n_{\sigma'}(\mathbf{r}')\}\right]}{\partial n_\sigma(\mathbf{r})} \right|_{n_\sigma(\mathbf{r})=n^0_\sigma(\mathbf{r})} , \end{aligned} \tag{41}$$

the minimization conditions lead to the Kohn-Sham equations.

Kohn-Sham equations

$$\begin{aligned} h^{\mathrm{KS}}_\sigma(\mathbf{r})\psi_n(\mathbf{r}) &= \epsilon_n(\mathbf{r})\psi_n(\mathbf{r}) \,, \\ h^{\mathrm{KS}}_\sigma(\mathbf{r}) &\equiv -\frac{\Delta_{\mathbf{r}}}{2m} + V^{\mathrm{KS}}_\sigma(\mathbf{r}) \,, \\ V^{\mathrm{KS}}_\sigma(\mathbf{r}) &\equiv U(\mathbf{r}) + V_{\mathrm{Har}}(\mathbf{r}) + v_{\mathrm{sp,xc},\sigma}(\mathbf{r}) \,. \end{aligned} \tag{42}$$

Density Functional Theory

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 $E_{\mathrm{sp,xc}}[\{n_\sigma(\mathbf{r})\}]$, 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 $E_{\mathrm{sp,xc}}[\{n_\sigma(\mathbf{r})\}]$.
Example: the local (spin) density approximation (L(S)DA).

Density Functional Theory for many-particle Hamiltonians

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 $\hat{H}_{\mathrm{kin}}$ plus the Hubbard interaction $\hat{V}_{\mathrm{loc}}$ define our new reference system,

$$\hat{H}_{\mathrm{kin}} \mapsto \hat{H}_{\mathrm{H}} = \hat{H}_{\mathrm{kin}} + \hat{V}_{\mathrm{loc}} - \hat{V}_{\mathrm{dc}} \,. \tag{43}$$

Here, $\hat{V}_{\mathrm{dc}}$ 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

$$F_{\mathrm{H}}\left[\{n_\sigma(\mathbf{r})\},\left\{|\Psi^{(n)}\rangle\right\}\right]=\langle\Psi^{(n)}|\hat{H}_{\mathrm{H}}|\Psi^{(n)}\rangle\ . \tag{44}$$

Its optimization provides $|\Psi^{(n)}_{\mathrm{H},0}\rangle$ and the functionals

$$\begin{aligned}
K_{\mathrm{H}}\left[\{n_\sigma(\mathbf{r})\}\right] &= \langle\Psi^{(n)}_{\mathrm{H},0}|\hat{H}_{\mathrm{kin}}|\Psi^{(n)}_{\mathrm{H},0}\rangle\ , \\
V_{\mathrm{loc/dc}}\left[\{n_\sigma(\mathbf{r})\}\right] &= \langle\Psi^{(n)}_{\mathrm{H},0}|\hat{V}_{\mathrm{loc/dc}}|\Psi^{(n)}_{\mathrm{H},0}\rangle\ , \qquad (45)\\
D_{\mathrm{H}}\left[\{n_\sigma(\mathbf{r})\}\right] &= K_{\mathrm{H}}\left[\{n_\sigma(\mathbf{r})\}\right]+U\left[\{n_\sigma(\mathbf{r})\}\right]+V_{\mathrm{Har}}\left[\{n_\sigma(\mathbf{r})\}\right] \\
&\quad +V_{\mathrm{loc}}\left[\{n_\sigma(\mathbf{r})\}\right]-V_{\mathrm{dc}}\left[\{n_\sigma(\mathbf{r})\}\right] \\
&\quad +E_{\mathrm{H,xc}}\left[\{n_\sigma(\mathbf{r})\}\right]\ . \qquad (46)
\end{aligned}$$

We demand $D_{\mathrm{H}}\left[\{n_\sigma(\mathbf{r})\}\right]=D\left[\{n_\sigma(\mathbf{r})\}\right]$. Then, $\hat{H}_{\mathrm{H}}$ leads to the exact ground-state energy E_0 and densities $n^0_\sigma(\mathbf{r})$.

Density Functional Theory for many-particle Hamiltonians

Problem

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

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

$$E = \langle \Psi | \hat{H}_{\mathrm{H}} | \Psi \rangle + U\left[\{n_\sigma(\mathbf{r})\}\right] + V_{\mathrm{Har}}\left[\{n_\sigma(\mathbf{r})\}\right] + E_{\mathrm{H,xc}}\left[\{n_\sigma(\mathbf{r})\}\right] , \tag{47}$$

we arrive at the many-particle Hubbard-Schrödinger equation

$$\left(\hat{H}_0 + \hat{V}_{\mathrm{loc}} - \hat{V}_{\mathrm{dc}}\right) |\Psi_0\rangle = E_0 |\Psi_0\rangle \tag{48}$$

with the single-particle Hamiltonian

$$\hat{H}_0 = \sum_\sigma \int \mathrm{d}\mathbf{r} \hat{\Psi}^\dagger_\sigma(\mathbf{r}) \left(-\frac{\Delta_{\mathbf{r}}}{2m} + U(\mathbf{r}) + V_{\mathrm{Har}}(\mathbf{r}) + v_{\mathrm{H,xc},\sigma}(\mathbf{r}) \right) \hat{\Psi}_\sigma(\mathbf{r}) . \tag{49}$$

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,

$$\begin{aligned} E_{\mathrm{H,xc}}\left[\{n_\sigma(\mathbf{r})\}\right] &= K\left[\{n_\sigma(\mathbf{r})\}\right] - K_{\mathrm{H}}\left[\{n_\sigma(\mathbf{r})\}\right] + E_{\mathrm{xc}}\left[\{n_\sigma(\mathbf{r})\}\right] \\ &\quad - \left(V_{\mathrm{loc}}\left[\{n_\sigma(\mathbf{r})\}\right] - V_{\mathrm{dc}}\left[\{n_\sigma(\mathbf{r})\}\right]\right) . \end{aligned} \tag{50}$$

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

Later, we shall employ the approximation

$$E_{\mathrm{H,xc}}\left[\{n_\sigma(\mathbf{r})\}\right] \approx E_{\mathrm{LDA,xc}}\left[\{n_\sigma(\mathbf{r})\}\right] . \tag{51}$$

Density Functional Theory for many-particle Hamiltonians

Approximate treatments

Idea: approximate the functional $\langle\Psi|\hat{H}_{\rm kin} + \hat{V}_{\rm loc} - \hat{V}_{\rm dc}|\Psi\rangle$.
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 $|\Psi_{\rm G}\rangle$.

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

$$|\Psi_{\rm G}\rangle = \hat{P}_{\rm G}|\Phi\rangle \quad , \quad \hat{P}_{\rm G} = \prod_{\mathbf{R}} \sum_{\Gamma} \lambda_{\mathbf{R};\Gamma}\, \hat{m}_{\mathbf{R};\Gamma} \; . \tag{52}$$

$\lambda_{\mathbf{R};\Gamma}$ are real variational parameters.

Density Functional Theory for many-particle Hamiltonians

The energy functional requires the evaluation of expectation values for the local interaction

$$V_{\mathrm{loc/dc}} = \sum_{\mathbf{R}} \sum_{\Gamma,\Gamma'} E^{\mathrm{loc/dc}}_{\Gamma,\Gamma'}(\mathbf{R}) \frac{\langle \Psi_{\mathrm{G}} | \hat{m}_{\mathbf{R};\Gamma,\Gamma'} | \Psi_{\mathrm{G}} \rangle}{\langle \Psi_{\mathrm{G}} | \Psi_{\mathrm{G}} \rangle} , \quad (53)$$

$$E^{\mathrm{loc/dc}}_{\Gamma,\Gamma'}(\mathbf{R}) = \langle \Gamma_{\mathbf{R}} | \hat{V}_{\mathrm{loc/dc}}(\mathbf{R}) | \Gamma'_{\mathbf{R}} \rangle , \quad (54)$$

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

$$\rho^{\mathrm{G}}_{(\mathbf{R}',b'),(\mathbf{R},b);\sigma} = \frac{\langle \Psi_{\mathrm{G}} | \hat{c}^\dagger_{\mathbf{R},b,\sigma} \hat{c}_{\mathbf{R}',b',\sigma} | \Psi_{\mathrm{G}} \rangle}{\langle \Psi_{\mathrm{G}} | \Psi_{\mathrm{G}} \rangle} . \quad (55)$$

Density Functional Theory for many-particle Hamiltonians

Gutzwiller energy functional

The Gutzwiller energy functional $E \equiv E\left[\{n_\sigma(\mathbf{r})\}, \{|\Psi_{\mathrm{G}}\rangle\}\right]$ reads

$$\begin{aligned} E &= \sum_{\mathbf{R},b,\mathbf{R}',b',\sigma} T_{(\mathbf{R},b),(\mathbf{R}',b');\sigma} \rho^{\mathrm{G}}_{(\mathbf{R}',b'),(\mathbf{R},b);\sigma} + V^{\mathrm{G}}_{\mathrm{loc}} - V^{\mathrm{G}}_{\mathrm{dc}} \\ &\quad + U\left[\{n_\sigma(\mathbf{r})\}\right] + V_{\mathrm{Har}}\left[\{n_\sigma(\mathbf{r})\}\right] + E_{\mathrm{H,xc}}\left[\{n_\sigma(\mathbf{r})\}\right] , \end{aligned} \tag{56}$$

$$T_{(\mathbf{R},b),(\mathbf{R}',b');\sigma} = \int \mathrm{d}\mathbf{r} \phi^*_{\mathbf{R},b,\sigma}(\mathbf{r}) \left(-\frac{\Delta_{\mathbf{r}}}{2m}\right) \phi_{\mathbf{R}',b',\sigma}(\mathbf{r}) . \tag{57}$$

The densities become

$$n_\sigma(\mathbf{r}) = \sum_{\mathbf{R},b,\mathbf{R}',b'} \phi^*_{\mathbf{R},b,\sigma}(\mathbf{r}) \phi_{\mathbf{R}',b',\sigma}(\mathbf{r}) \rho^{\mathrm{G}}_{(\mathbf{R}',b'),(\mathbf{R},b);\sigma} . \tag{58}$$

Density Functional Theory for many-particle Hamiltonians

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 $C_{b',b;\sigma}(\mathbf{R}) = \langle \Phi | \hat{c}^{\dagger}_{\mathbf{R},b,\sigma} \hat{c}_{\mathbf{R},b',\sigma} | \Phi \rangle$ and the Gutzwiller variational parameters $\lambda_{\Gamma,\Gamma'}(\mathbf{R})$. For example,

$$V^{\mathrm{G}}_{\mathrm{loc}} = \sum_{\mathbf{R}} \sum_{\Gamma,\Gamma'} \lambda_{\mathbf{R};\Gamma} E^{\mathrm{loc}}_{\mathbf{R};\Gamma,\Gamma'} \langle \hat{m}_{\mathbf{R};\Gamma,\Gamma'} \rangle_{\Phi} \lambda_{\mathbf{R};\Gamma'} \,. \tag{59}$$

Density Functional Theory for many-particle Hamiltonians

For $\mathbf{R} \neq \mathbf{R}'$, the correlated single-particle density matrix becomes

$$\rho^{\mathrm{G}}_{(\mathbf{R}',b'),(\mathbf{R},b);\sigma} = \sum_{a,a'} q^{a,\sigma}_{b,\sigma}(\mathbf{R}) \left(q^{a',\sigma}_{b',\sigma}(\mathbf{R}')\right)^* \rho_{(\mathbf{R}',a'),(\mathbf{R},a);\sigma} \,. \qquad (60)$$

The orbital-dependent factors $q^{a,\sigma}_{b,\sigma}(\mathbf{R})$ 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' $\oplus$ '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

$$\hat{H}^{\mathrm{G}}_{\mathrm{qp}} = \sum_{\mathbf{k},b,b',\sigma} h^{\mathrm{G}}_{b,b';\sigma}(\mathbf{k}) \hat{c}^{\dagger}_{\mathbf{k},b,\sigma} \hat{c}_{\mathbf{k},b',\sigma} \tag{61}$$

with the matrix elements in the orbital Bloch basis

$$\begin{aligned} h^{\mathrm{G}}_{b,b';\sigma}(\mathbf{k}) &= \eta_{b,b';\sigma} + \sum_{a,a'} q^{b,\sigma}_{a,\sigma} \left(q^{b',\sigma}_{a',\sigma} \right)^{*} h^{0}_{a,a';\sigma}(\mathbf{k}) \,, \\ h^{0}_{a,a';\sigma}(\mathbf{k}) &= \int \mathrm{d}\mathbf{r} \phi^{*}_{\mathbf{k},a,\sigma}(\mathbf{r}) \left(-\frac{\Delta_{\mathbf{r}}}{2m} + V^{\mathrm{H}}_{\sigma}(\mathbf{r}) \right) \phi_{\mathbf{k},a',\sigma}(\mathbf{r}) \,, \\ V^{\mathrm{H}}_{\sigma}(\mathbf{r}) &= U(\mathbf{r}) + V_{\mathrm{Har}}(\mathbf{r}) + v_{\mathrm{H,xc},\sigma}(\mathbf{r}) \,. \end{aligned} \tag{62}$$

$\eta_{b,b';\sigma}$: Lagrange parameters (variational band-shifts).

Transition metals

In cubic symmetry, the local interaction for $3d$ electrons reads

$$\begin{aligned}
\hat{V}_{\mathrm{loc}}^{\mathrm{full}} &= \hat{V}_{\mathrm{loc}}^{\mathrm{dens}} + \hat{V}_{\mathrm{loc}}^{\mathrm{sf}} + \hat{V}_{\mathrm{loc}}^{(3)} + \hat{V}_{\mathrm{loc}}^{(4)} \;, \\
\hat{V}_{\mathrm{loc}}^{\mathrm{dens}} &= \sum_{c,\sigma} U(c,c)\hat{n}_{c,\sigma}\hat{n}_{c,\bar{\sigma}} + \sum_{c(\neq)c'} \sum_{\sigma,\sigma'} \widetilde{U}_{\sigma,\sigma'}(c,c')\hat{n}_{c,\sigma}\hat{n}_{c',\sigma'} \;, \\
\hat{V}_{\mathrm{loc}}^{\mathrm{sf}} &= \sum_{c(\neq)c'} J(c,c') \left(\hat{c}^{\dagger}_{c,\uparrow}\hat{c}^{\dagger}_{c,\downarrow}\hat{c}_{c',\downarrow}\hat{c}_{c',\uparrow} + \mathrm{h.c.} \right) \\
&\quad + \sum_{c(\neq)c';\sigma} J(c,c')\hat{c}^{\dagger}_{c,\sigma}\hat{c}^{\dagger}_{c',\bar{\sigma}}\hat{c}_{c,\bar{\sigma}}\hat{c}_{c',\sigma} \;. \qquad (63)
\end{aligned}$$

Here, $\bar{\uparrow} = \downarrow$ ($\bar{\downarrow} = \uparrow$) and $\widetilde{U}_{\sigma,\sigma'}(c,c') = U(c,c) - \delta_{\sigma,\sigma'}J(c,c')$. $U \equiv U(c,c)/2$ and $J \equiv J(c,c')$ are local Hubbard and Hund's-rule exchange interactions. DMFT calculations often employ $\hat{V}_{\mathrm{loc}}^{\mathrm{dens}}$ only (reduction of the numerical effort).

Transition metals

Gutzwiller calculations include the full $\hat{V}_{\mathrm{loc}}$ with the spin-flip terms and the three-orbital and four-orbital terms

$$\begin{aligned}\hat{V}^{(3)}_{\mathrm{loc}} &= \sum_{t;\sigma,\sigma'} (T(t) - \delta_{\sigma,\sigma'} A(t)) \hat{n}_{t,\sigma} \hat{c}^{\dagger}_{u,\sigma'} \hat{c}_{v,\sigma'} + \mathrm{h.c.}\,, \qquad (64)\\ &\quad + \sum_{t,\sigma} A(t) \left(\hat{c}^{\dagger}_{t,\sigma} \hat{c}^{\dagger}_{t,\bar{\sigma}} \hat{c}_{u,\bar{\sigma}} \hat{c}_{v,\sigma} + \hat{c}^{\dagger}_{t,\sigma} \hat{c}^{\dagger}_{u,\bar{\sigma}} \hat{c}_{t,\bar{\sigma}} \hat{c}_{v,\sigma} + \mathrm{h.c.} \right)\\ \hat{V}^{(4)}_{\mathrm{loc}} &= \sum_{t(\neq)t'(\neq)t''} \sum_{e,\sigma,\sigma'} S(t,t';t'',e) \hat{c}^{\dagger}_{t,\sigma} \hat{c}^{\dagger}_{t',\sigma'} \hat{c}_{t'',\sigma'} \hat{c}_{e,\sigma} + \mathrm{h.c.}\,.\end{aligned}$$

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 $v = x^2 - y^2$.

Transition metals

Double counting corrections

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

$$V_{\mathrm{dc}}^{\mathrm{LDA}+U} = \frac{U}{2}\bar{n}(\bar{n}-1) - \frac{J}{2}\sum_{\sigma}\bar{n}_{\sigma}(1-\bar{n}_{\sigma})\,, \tag{65}$$

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

$$\eta_{c,c;\sigma}^{\mathrm{dc}} = -\left[U\left(\bar{n}-1/2\right) + J\left(\bar{n}_{\sigma}-1/2\right)\right]\,. \tag{66}$$

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 $3d$-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.

Transition metals

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

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

$$\rho^{\mathrm{G}}_{(\mathbf{R},b'),(\mathbf{R},b);\sigma} = \delta_{b,b'} \rho_{(\mathbf{R},b),(\mathbf{R},b);\sigma} . \quad (68)$$

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.

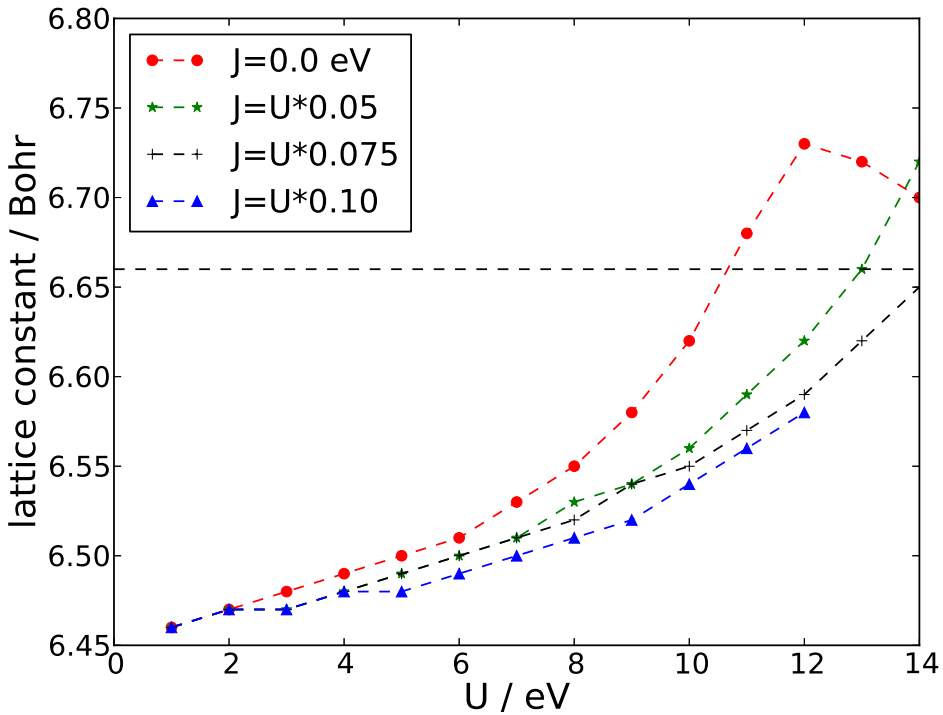

Fig. 2: Fcc lattice constant of nickel as a function of U for different values of J/U, calculated with the full local Hamiltonian $\hat{V}_{\mathrm{loc}}^{\mathrm{full}}$ and the LDA+U double counting correction; dashed line: experimental value.

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

Transition metals

In order to fix both U and J, we must also consider the spin-only magnetic moment.

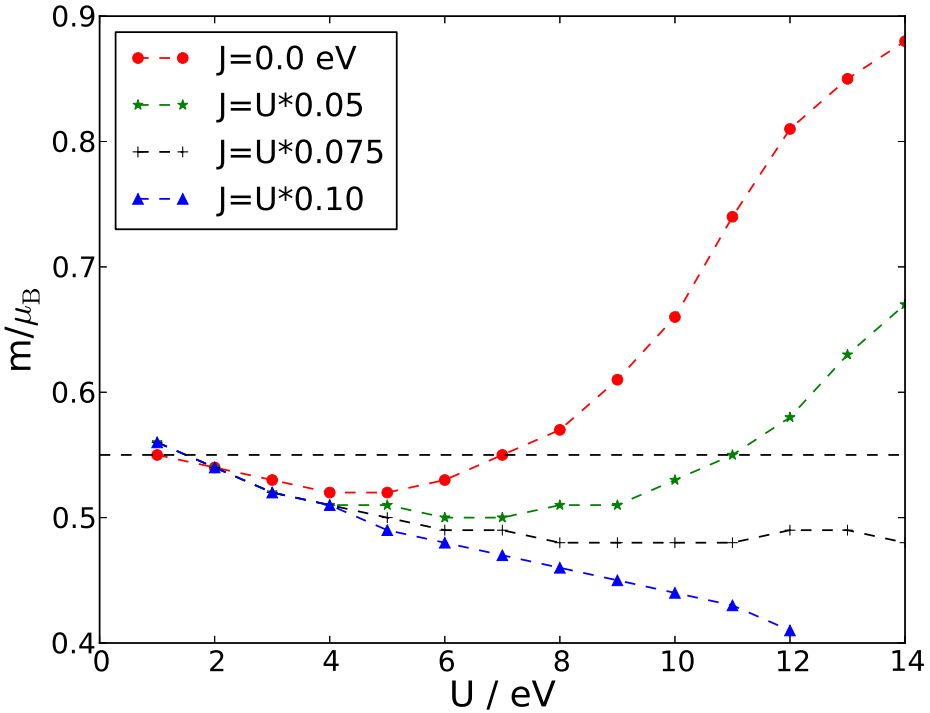

Fig. 3: Magnetic moment of nickel as a function of U for different values of J/U, calculated with the full local Hamiltonian $\hat{V}_{\mathrm{loc}}^{\mathrm{full}}$ and the LDA+U double counting correction; dashed line: experimental value.

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

Transition metals

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

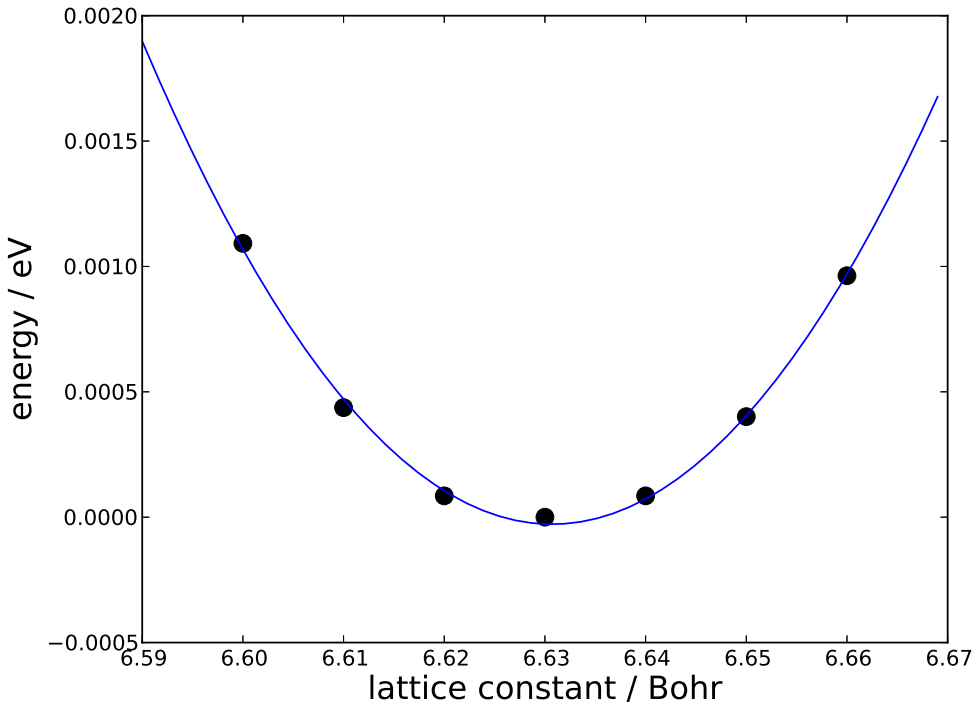

Fig. 4: Ground-state energy per particle $E_0(a)/N$ relative to its value at $a = 6.63 a_{\mathrm{B}}$ as a function of the fcc lattice parameter a/a_{B}, calculated with the full local Hamiltonian $\hat{V}^{\mathrm{full}}_{\mathrm{loc}}$ and the LDA+U double counting correction; full line: 2^{nd}-order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

$K_{\mathrm{G}} = 169\,\mathrm{GPa}$, in good agreement with experiment,
$K = 182\,\mathrm{GPa}$, whereas $K_{\mathrm{DFT}} = 245\,\mathrm{GPa}$.

Transition metals

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

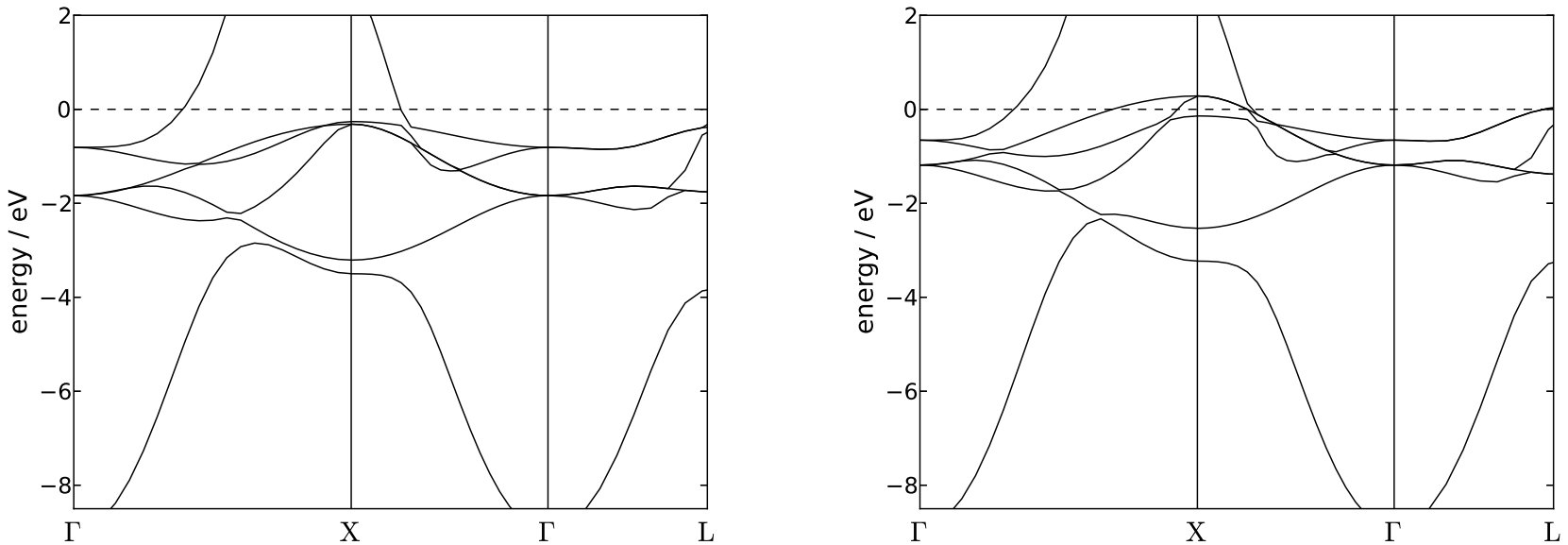

Fig. 5: Landau-Gutzwiller quasi-particle band structure of fcc nickel along high-symmetry lines in the first Brillouin zone, calculated with the full local Hamiltonian and the LDA+U double-counting correction; left: majority spin; right: minority spin. Fermi energy $E_{\mathrm{F}}^{\mathrm{G}} = 0$.

Transition metals

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

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 ($W_{\mathrm{G-DFT}} = 3.3\,\mathrm{eV}$, whereas $W_{\mathrm{DFT}} = 4.5\,\mathrm{eV}$).
- 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.

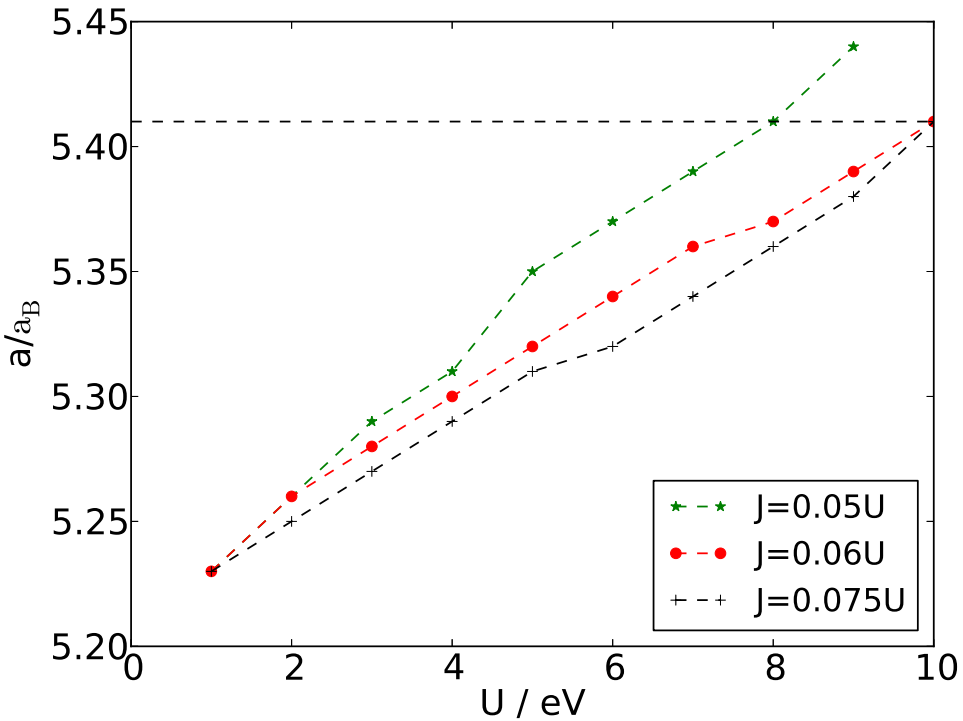

Fig. 6: Bcc lattice constant of iron as a function of U for different values of J/U, calculated with the full local Hamiltonian $\hat{V}^{\mathrm{full}}_{\mathrm{loc}}$ and the LDA+U double counting correction; dashed line: experimental value.

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

Transition metals

In order to fix both U and J, we must also consider the spin-only magnetic moment.

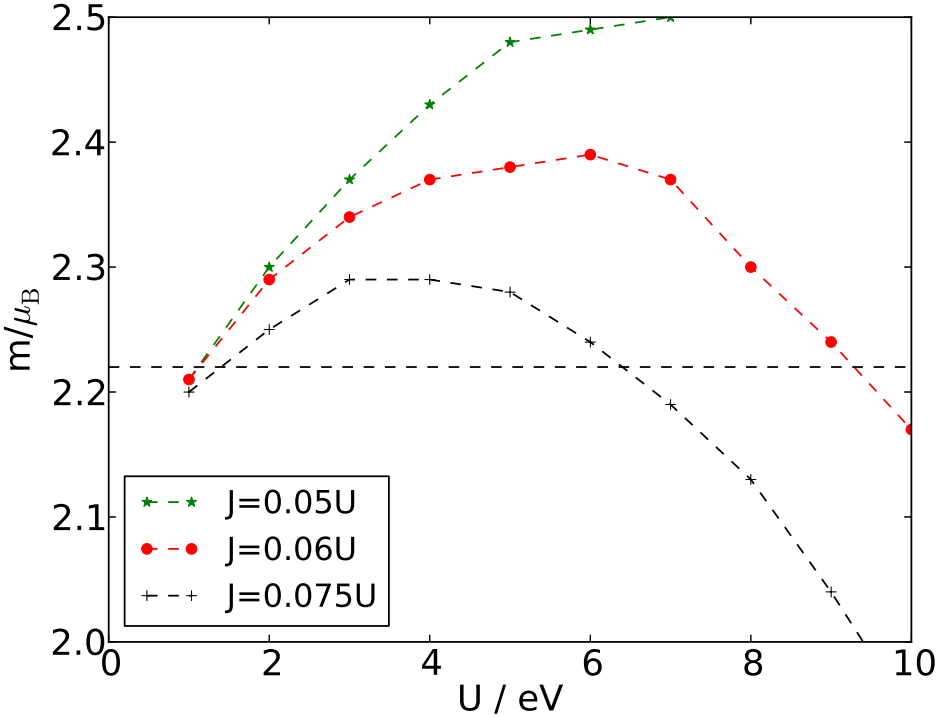

Fig. 7: Magnetic moment of iron as a function of U for different values of J/U, calculated with the full local Hamiltonian $\hat{V}_{\mathrm{loc}}^{\mathrm{full}}$ and the LDA+U double counting correction; dashed line: experimental value.

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

Transition metals

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

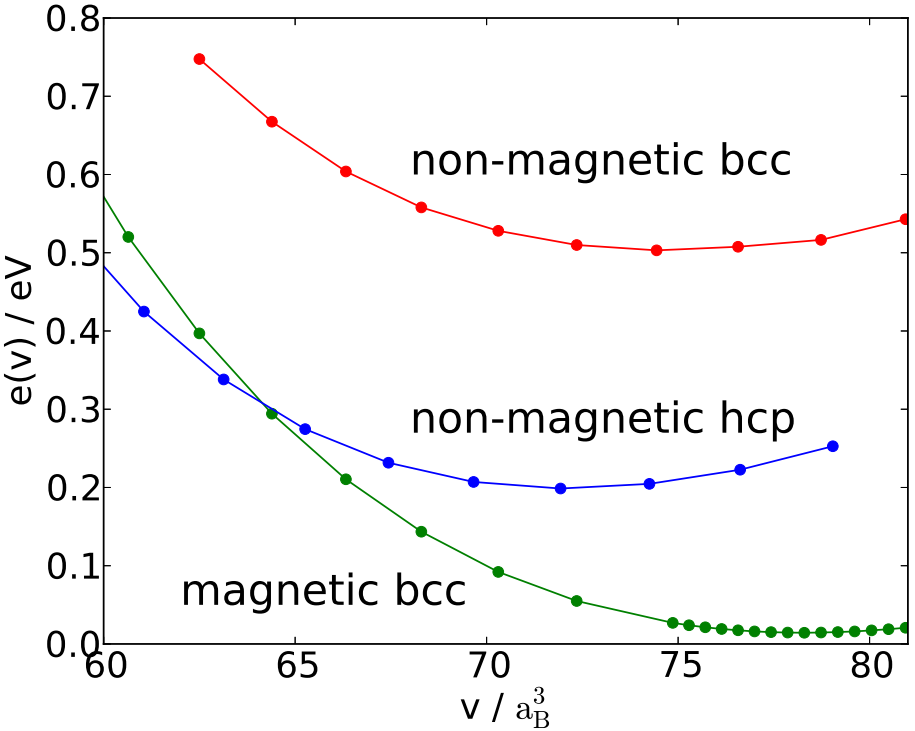

Fig. 8: Energy per atom $e(v)$ in units of eV as a function of the unit-cell volume v in units of a_{B}^3 for non-magnetic and ferromagnetic bcc iron and non-magnetic hcp iron at $U = 9\,\mathrm{eV}$ and $J = 0.54\,\mathrm{eV}$ and ambient pressure. The energies are shifted by the same value.

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

Transition metals

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

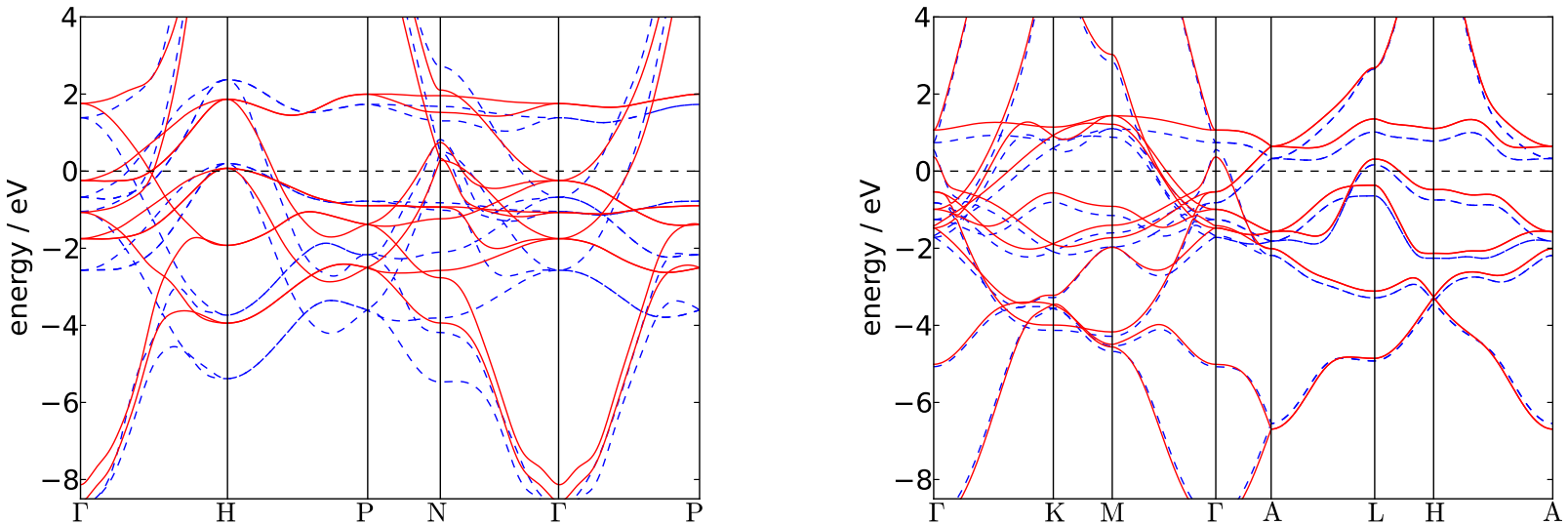

Fig. 9: Landau-Gutzwiller quasi-particle band structure (full lines) and DFT(LDA) bands (dashed lines) of bcc iron (left) and hcp iron (right) along high-symmetry lines in the first Brillouin zone, calculated with the full local Hamiltonian and the LDA+U double-counting correction; Fermi energy $E_{\mathrm{F}}^{\mathrm{G}}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

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 $(U = 13\,\mathrm{eV}, J = 0.9\,\mathrm{eV})_{\mathrm{Ni}}$ and $(U = 9\,\mathrm{eV}, J = 0.54\,\mathrm{eV})_{\mathrm{Fe}}$.
  - 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.

Thanks

Thank you for your attention!