

Gutzwiller Density Functional Theory

Florian Gebhard

Department of Physics, Philipps-Universität Marburg, Germany

in collaboration with
Jörg Bünemann, Marburg
Tobias Schickling, Marburg
Werner Weber, Dortmund

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Density Functional Theory

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

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

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

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

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

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

$$U(\mathbf{r}) = \sum_{\mathbf{R}} \frac{e^2}{|\mathbf{r} - \mathbf{R}|}. \quad (3)$$

Density Functional Theory

Ritz variational principle

Task: minimize the energy functional

$$E[\{|\Psi\rangle\}] = \frac{\langle\Psi|\hat{H}|\Psi\rangle}{\langle\Psi|\Psi\rangle}. \quad (4)$$

Problem

This task poses a difficult many-body problem!

Density Functional Theory

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

$$n_{\sigma}(\mathbf{r}) = \langle \Psi^{(n)} | \hat{\Psi}_{\sigma}^{\dagger}(\mathbf{r}) \hat{\Psi}_{\sigma}(\mathbf{r}) | \Psi^{(n)} \rangle . \quad (5)$$

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

$$\hat{H}_{\text{kin}} = \sum_{\sigma} \int d\mathbf{r} \hat{\Psi}_{\sigma}^{\dagger}(\mathbf{r}) \left(-\frac{\Delta_{\mathbf{r}}}{2m} \right) \hat{\Psi}_{\sigma}(\mathbf{r}) , \quad (6)$$

$$\begin{aligned} \hat{V}_{\text{xc}} = \sum_{\sigma, \sigma'} \int d\mathbf{r} \int d\mathbf{r}' V(\mathbf{r} - \mathbf{r}') & \left[\hat{\Psi}_{\sigma}^{\dagger}(\mathbf{r}) \hat{\Psi}_{\sigma'}^{\dagger}(\mathbf{r}') \hat{\Psi}_{\sigma'}(\mathbf{r}') \hat{\Psi}_{\sigma}(\mathbf{r}) \right. \\ & \left. - 2 \hat{\Psi}_{\sigma}^{\dagger}(\mathbf{r}) \hat{\Psi}_{\sigma}(\mathbf{r}) n_{\sigma'}(\mathbf{r}') + n_{\sigma}(\mathbf{r}) n_{\sigma'}(\mathbf{r}') \right] . \end{aligned}$$

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

$$F \left[\{n_\sigma(\mathbf{r})\}, \{|\Psi^{(n)}\rangle\} \right] = \langle \Psi^{(n)} | \hat{H}_{\text{kin}} + \hat{V}_{\text{xc}} | \Psi^{(n)} \rangle . \quad (7)$$

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,

$$\text{Kinetic:} \quad K[\{n_\sigma(\mathbf{r})\}] = \langle \Psi_0^{(n)} | \hat{H}_{\text{kin}} | \Psi_0^{(n)} \rangle , \quad (8)$$

$$\text{Exchange-correlation:} \quad E_{\text{xc}}[\{n_\sigma(\mathbf{r})\}] = \langle \Psi_0^{(n)} | \hat{V}_{\text{xc}} | \Psi_0^{(n)} \rangle . \quad (9)$$

Density Functional Theory

Density Functional

Task: minimize the Density Functional

$$D[\{n_\sigma(\mathbf{r})\}] = K[\{n_\sigma(\mathbf{r})\}] + E_{\text{xc}}[\{n_\sigma(\mathbf{r})\}] + U[\{n_\sigma(\mathbf{r})\}] + V_{\text{Har}}[\{n_\sigma(\mathbf{r})\}] \quad (10)$$

with the ionic/Hartree energies

$$\text{Ionic: } U[\{n_\sigma(\mathbf{r})\}] = \sum_\sigma \int d\mathbf{r} U(\mathbf{r}) n_\sigma(\mathbf{r}), \quad (11)$$

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

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

Density Functional Theory

Problem

The minimization of the energy functional in eq. (7) ● poses a 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.

Density Functional Theory

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

$$n_{\sigma}^{\text{SP}}(\mathbf{r}) = \langle \Phi^{(n)} | \hat{\Psi}_{\sigma}^{\dagger}(\mathbf{r}) \hat{\Psi}_{\sigma}(\mathbf{r}) | \Phi^{(n)} \rangle . \quad (12)$$

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

$$F_{\text{sp}} \left[\{n_{\sigma}^{\text{SP}}(\mathbf{r})\}, \{|\Phi^{(n)}\rangle\} \right] = \langle \Phi^{(n)} | \hat{H}_{\text{kin}} | \Phi^{(n)} \rangle . \quad (13)$$

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

$$K_{\text{sp}} [\{n_{\sigma}^{\text{SP}}(\mathbf{r})\}] = \langle \Phi_0^{(n)} | \hat{H}_{\text{kin}} | \Phi_0^{(n)} \rangle . \quad (14)$$

Density Functional Theory

The single-particle density functional is *defined* as

$$D_{\text{sp}} [\{n_{\sigma}^{\text{sp}}(\mathbf{r})\}] = K_{\text{sp}} [\{n_{\sigma}^{\text{sp}}(\mathbf{r})\}] + U [\{n_{\sigma}^{\text{sp}}(\mathbf{r})\}] + V_{\text{Har}} [\{n_{\sigma}^{\text{sp}}(\mathbf{r})\}] + E_{\text{sp,xc}} [\{n_{\sigma}^{\text{sp}}(\mathbf{r})\}] \quad (15)$$

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

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

$$n_{\sigma}^{\text{sp}}(\mathbf{r}) = n_{\sigma}(\mathbf{r}) . \quad (16)$$

Density Functional Theory

Hohenberg-Kohn theorem

We demand

$$D_{\text{sp}} [\{n_{\sigma}(\mathbf{r})\}] = D [\{n_{\sigma}(\mathbf{r})\}]. \quad (17)$$

\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. (17), we *define*

$$E_{\text{sp,xc}} [\{n_{\sigma}(\mathbf{r})\}] = K [\{n_{\sigma}(\mathbf{r})\}] - K_{\text{sp}} [\{n_{\sigma}(\mathbf{r})\}] + E_{\text{xc}} [\{n_{\sigma}(\mathbf{r})\}]. \quad (18)$$

Problem

We know neither of the quantities on the r.h.s. of eq. (18)!

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

$$E[\{n_\sigma(\mathbf{r})\}, \{|\Phi\rangle\}] = \langle \Phi | \hat{H}_{\text{kin}} | \Phi \rangle + U[\{n_\sigma(\mathbf{r})\}] \quad (19)$$

$$+ V_{\text{Har}}[\{n_\sigma(\mathbf{r})\}] + E_{\text{sp,xc}}[\{n_\sigma(\mathbf{r})\}] .$$

Remaining task:

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

$$\hat{\Psi}_\sigma^\dagger(\mathbf{r}) = \sum_n \psi_n^*(\mathbf{r}) \hat{b}_{n,\sigma}^\dagger, \quad \hat{\Psi}_\sigma(\mathbf{r}) = \sum_n \psi_n(\mathbf{r}) \hat{b}_{n,\sigma}. \quad (20)$$

Density Functional Theory

With the Hartree and exchange-correlation potentials

$$\begin{aligned}
 V_{\text{Har}}(\mathbf{r}) &\equiv \sum_{\sigma'} \int d\mathbf{r}' 2V(\mathbf{r} - \mathbf{r}') n_{\sigma'}^0(\mathbf{r}') , \\
 v_{\text{sp,xc},\sigma}(\mathbf{r}) &\equiv \left. \frac{\partial E_{\text{sp,xc}}[\{n_{\sigma'}(\mathbf{r}')\}]}{\partial n_{\sigma}(\mathbf{r})} \right|_{n_{\sigma}(\mathbf{r})=n_{\sigma}^0(\mathbf{r})} , \quad (21)
 \end{aligned}$$

the minimization conditions lead to the Kohn-Sham equations.

Kohn-Sham equations

$$\begin{aligned}
 h_{\sigma}^{\text{KS}}(\mathbf{r})\psi_n(\mathbf{r}) &= \epsilon_n(\mathbf{r})\psi_n(\mathbf{r}) , \\
 h_{\sigma}^{\text{KS}}(\mathbf{r}) &\equiv -\frac{\Delta_{\mathbf{r}}}{2m} + V_{\sigma}^{\text{KS}}(\mathbf{r}) , \\
 V_{\sigma}^{\text{KS}}(\mathbf{r}) &\equiv U(\mathbf{r}) + V_{\text{Har}}(\mathbf{r}) + v_{\text{sp,xc},\sigma}(\mathbf{r}) .
 \end{aligned} \quad (22)$$

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 $E_{\text{sp,xc}}[\{n_{\sigma}(\mathbf{r})\}]$, 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 $E_{\text{sp,xc}}[\{n_{\sigma}(\mathbf{r})\}]$.
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}_{kin} plus the Hubbard interaction \hat{V}_{loc} define our new reference system,

$$\hat{H}_{\text{kin}} \mapsto \hat{H}_{\text{H}} = \hat{H}_{\text{kin}} + \hat{V}_{\text{loc}} - \hat{V}_{\text{dc}}. \quad (23)$$

Here, \hat{V}_{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

$$F_H \left[\{n_\sigma(\mathbf{r})\}, \left\{ |\Psi^{(n)}\rangle \right\} \right] = \langle \Psi^{(n)} | \hat{H}_H | \Psi^{(n)} \rangle . \quad (24)$$

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

$$K_H \left[\{n_\sigma(\mathbf{r})\} \right] = \langle \Psi_{H,0}^{(n)} | \hat{H}_{\text{kin}} | \Psi_{H,0}^{(n)} \rangle ,$$

$$V_{\text{loc/dc}} \left[\{n_\sigma(\mathbf{r})\} \right] = \langle \Psi_{H,0}^{(n)} | \hat{V}_{\text{loc/dc}} | \Psi_{H,0}^{(n)} \rangle , \quad (25)$$

$$\begin{aligned} D_H \left[\{n_\sigma(\mathbf{r})\} \right] &= K_H \left[\{n_\sigma(\mathbf{r})\} \right] + U \left[\{n_\sigma(\mathbf{r})\} \right] + V_{\text{Har}} \left[\{n_\sigma(\mathbf{r})\} \right] \\ &\quad + V_{\text{loc}} \left[\{n_\sigma(\mathbf{r})\} \right] - V_{\text{dc}} \left[\{n_\sigma(\mathbf{r})\} \right] \\ &\quad + E_{H,\text{xc}} \left[\{n_\sigma(\mathbf{r})\} \right] . \end{aligned} \quad (26)$$

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

Density Functional Theory for many-particle Hamiltonians

Problem

The Hubbard interaction \hat{V}_{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

$$E = \langle \Psi | \hat{H}_{\text{H}} | \Psi \rangle + U[\{n_{\sigma}(\mathbf{r})\}] + V_{\text{Har}}[\{n_{\sigma}(\mathbf{r})\}] + E_{\text{H,xc}}[\{n_{\sigma}(\mathbf{r})\}], \quad (27)$$

we arrive at the many-particle Hubbard-Schrödinger equation

$$(\hat{H}_0 + \hat{V}_{\text{loc}} - \hat{V}_{\text{dc}}) |\Psi_0\rangle = E_0 |\Psi_0\rangle \quad (28)$$

with the single-particle Hamiltonian

$$\hat{H}_0 = \sum_{\sigma} \int d\mathbf{r} \hat{\Psi}_{\sigma}^{\dagger}(\mathbf{r}) \left(-\frac{\Delta_{\mathbf{r}}}{2m} + U(\mathbf{r}) + V_{\text{Har}}(\mathbf{r}) + v_{\text{H,xc},\sigma}(\mathbf{r}) \right) \hat{\Psi}_{\sigma}(\mathbf{r}). \quad (29)$$

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,

$$E_{H,xc} [\{n_\sigma(\mathbf{r})\}] = K [\{n_\sigma(\mathbf{r})\}] - K_H [\{n_\sigma(\mathbf{r})\}] + E_{xc} [\{n_\sigma(\mathbf{r})\}] - (V_{loc} [\{n_\sigma(\mathbf{r})\}] - V_{dc} [\{n_\sigma(\mathbf{r})\}]) . \quad (30)$$

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

Later, we shall employ the approximation

$$E_{H,xc} [\{n_\sigma(\mathbf{r})\}] \approx E_{LDA,xc} [\{n_\sigma(\mathbf{r})\}] . \quad (31)$$

Density Functional Theory for many-particle Hamiltonians

Variational approach

Idea:

approximate the many-particle functional $\langle \Psi | \hat{H}_{\text{kin}} + \hat{V}_{\text{loc}} - \hat{V}_{\text{dc}} | \Psi \rangle$.

Strategies:

- LDA+ U : use single-particle states $|\Phi\rangle$.
- Gutzwiller: use many-particle variational states $|\Psi_G\rangle$.

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

$$|\Psi_G\rangle = \hat{P}_G |\Phi\rangle \quad , \quad \hat{P}_G = \prod_{\mathbf{R}} \sum_{\Gamma,\Gamma'} \lambda_{\Gamma,\Gamma'}(\mathbf{R}) \hat{m}_{\mathbf{R};\Gamma,\Gamma'} \quad (32)$$

$\lambda_{\Gamma,\Gamma'}(\mathbf{R})$ are, in general, complex variational parameters.

Density Functional Theory for many-particle Hamiltonians

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

$$V_{\text{loc/dc}} = \sum_{\mathbf{R}} \sum_{\Gamma, \Gamma'} E_{\Gamma, \Gamma'}^{\text{loc/dc}}(\mathbf{R}) \frac{\langle \Psi_G | \hat{m}_{\mathbf{R}; \Gamma, \Gamma'} | \Psi_G \rangle}{\langle \Psi_G | \Psi_G \rangle}, \quad (33)$$

$$E_{\Gamma, \Gamma'}^{\text{loc/dc}}(\mathbf{R}) = \mathbf{R} \langle \Gamma | \hat{V}_{\text{loc/dc}}(\mathbf{R}) | \Gamma' \rangle_{\mathbf{R}}, \quad (34)$$

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

$$\rho_{(\mathbf{R}', b'), (\mathbf{R}, b); \sigma}^G = \frac{\langle \Psi_G | \hat{c}_{\mathbf{R}, b, \sigma}^{\dagger} \hat{c}_{\mathbf{R}', b', \sigma} | \Psi_G \rangle}{\langle \Psi_G | \Psi_G \rangle}. \quad (35)$$

Density Functional Theory for many-particle Hamiltonians

Gutzwiller energy functional

The Gutzwiller energy functional $E \equiv E [\{n_\sigma(\mathbf{r})\}, \{|\Psi_G\rangle\}]$ reads

$$E = \sum_{\mathbf{R},b,\mathbf{R}',b',\sigma} T_{(\mathbf{R},b),(\mathbf{R}',b');\sigma} \rho_{(\mathbf{R}',b'),(\mathbf{R},b);\sigma}^G + V_{\text{loc}}^G - V_{\text{dc}}^G \\ + U[\{n_\sigma(\mathbf{r})\}] + V_{\text{Har}}[\{n_\sigma(\mathbf{r})\}] + E_{\text{H,xc}}[\{n_\sigma(\mathbf{r})\}], \quad (36)$$

$$T_{(\mathbf{R},b),(\mathbf{R}',b');\sigma} = \int d\mathbf{r} \phi_{\mathbf{R},b,\sigma}^*(\mathbf{r}) \left(-\frac{\Delta_{\mathbf{r}}}{2m} \right) \phi_{\mathbf{R}',b',\sigma}(\mathbf{r}). \quad (37)$$

The densities become

$$n_\sigma(\mathbf{r}) = \sum_{\mathbf{R},b,\mathbf{R}',b'} \phi_{\mathbf{R},b,\sigma}^*(\mathbf{r}) \phi_{\mathbf{R}',b',\sigma}(\mathbf{r}) \rho_{(\mathbf{R}',b'),(\mathbf{R},b);\sigma}^G. \quad (38)$$

Density Functional Theory for many-particle Hamiltonians

Problem

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

Solution

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

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

$$V_{\text{loc}}^{\text{G}} = \sum_{\mathbf{R}} \sum_{\Gamma_1, \dots, \Gamma_4} \lambda_{\Gamma_2, \Gamma_1}^*(\mathbf{R}) E_{\Gamma_2, \Gamma_3}^{\text{loc}}(\mathbf{R}) \lambda_{\Gamma_3, \Gamma_4}(\mathbf{R}) \langle \hat{m}_{\mathbf{R}; \Gamma_1, \Gamma_4} \rangle_{\Phi}. \quad (39)$$

Density Functional Theory for many-particle Hamiltonians

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

$$\rho_{(\mathbf{R}',b'),(\mathbf{R},b);\sigma}^{\text{G}} = \sum_{a,a'} q_{b,\sigma}^{a,\sigma}(\mathbf{R}) (q_{b',\sigma'}^{a',\sigma}(\mathbf{R}'))^* \rho_{(\mathbf{R}',a'),(\mathbf{R},a);\sigma} \quad (40)$$

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

Results

- In the limit $Z \rightarrow \infty$, the Gutzwiller many-body problem is solved without further approximations.
- 'Solve the Gutzwiller–Kohn–Sham equations' \oplus
'Minimize with respect to the Gutzwiller parameters $\lambda_{\Gamma,\Gamma'}(\mathbf{R})$ ' is similar in complexity to the DFT. For simple systems such as nickel, the latter minimization is computationally inexpensive (20% of total CPU time).

Translational invariant lattice systems

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

$$\hat{H}_{\text{QP}}^{\text{G}} = \sum_{\mathbf{k}, b, b', \sigma} h_{b, b'; \sigma}^{\text{G}}(\mathbf{k}) \hat{c}_{\mathbf{k}, b, \sigma}^{\dagger} \hat{c}_{\mathbf{k}, b', \sigma} \quad (41)$$

with the matrix elements in the orbital Bloch basis

$$h_{b, b'; \sigma}^{\text{G}}(\mathbf{k}) = \eta_{b, b'; \sigma} + \sum_{a, a'} q_{a, \sigma}^{b, \sigma} \left(q_{a', \sigma}^{b', \sigma} \right)^* h_{a, a'; \sigma}^0(\mathbf{k}),$$

$$h_{a, a'; \sigma}^0(\mathbf{k}) = \int d\mathbf{r} \phi_{\mathbf{k}, a, \sigma}^*(\mathbf{r}) \left(-\frac{\Delta_{\mathbf{r}}}{2m} + V_{\sigma}^{\text{H}}(\mathbf{r}) \right) \phi_{\mathbf{k}, a', \sigma}(\mathbf{r}), \quad (42)$$

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

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

Translational invariant lattice systems

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

$$\begin{aligned}
 \hat{V}_{\text{loc}}^{\text{full}} &= \hat{V}_{\text{loc}}^{\text{dens}} + \hat{V}_{\text{loc}}^{\text{sf}} + \hat{V}_{\text{loc}}^{(3)} + \hat{V}_{\text{loc}}^{(4)}, \\
 \hat{V}_{\text{loc}}^{\text{dens}} &= \sum_{c,\sigma} U(c, c) \hat{n}_{c,\sigma} \hat{n}_{c',\bar{\sigma}} + \sum_{c(\neq)c'} \sum_{\sigma,\sigma'} \tilde{U}_{\sigma,\sigma'}(c, c') \hat{n}_{c,\sigma} \hat{n}_{c',\sigma'}, \\
 \hat{V}_{\text{loc}}^{\text{sf}} &= \sum_{c(\neq)c'} J(c, c') \left(\hat{c}_{c,\uparrow}^\dagger \hat{c}_{c,\downarrow}^\dagger \hat{c}_{c',\downarrow} \hat{c}_{c',\uparrow} + \text{h.c.} \right) \\
 &\quad + \sum_{c(\neq)c';\sigma} J(c, c') \hat{c}_{c,\sigma}^\dagger \hat{c}_{c',\bar{\sigma}}^\dagger \hat{c}_{c,\bar{\sigma}} \hat{c}_{c',\sigma}. \tag{43}
 \end{aligned}$$

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

Translational invariant lattice systems

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

$$\begin{aligned} \hat{V}_{\text{loc}}^{(3)} &= \sum_{t;\sigma,\sigma'} (T(t) - \delta_{\sigma,\sigma'} A(t)) \hat{n}_{t,\sigma} \hat{c}_{u,\sigma'}^\dagger \hat{c}_{v,\sigma'} + \text{h.c.} , & (44) \\ &+ \sum_{t,\sigma} A(t) \left(\hat{c}_{t,\sigma}^\dagger \hat{c}_{t,\bar{\sigma}}^\dagger \hat{c}_{u,\bar{\sigma}} \hat{c}_{v,\sigma} + \hat{c}_{t,\sigma}^\dagger \hat{c}_{u,\bar{\sigma}}^\dagger \hat{c}_{t,\bar{\sigma}} \hat{c}_{v,\sigma} + \text{h.c.} \right) \\ \hat{V}_{\text{loc}}^{(4)} &= \sum_{t(\neq)t'(\neq)t''} \sum_{e,\sigma,\sigma'} S(t, t'; t'', e) \hat{c}_{t,\sigma}^\dagger \hat{c}_{t',\sigma'}^\dagger \hat{c}_{t'',\sigma'} \hat{c}_{e,\sigma} + \text{h.c.} . \end{aligned}$$

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

Translational invariant lattice systems

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

$$V_{\text{dc}}^{\text{LDA}+U} = \frac{U}{2} \bar{n}(\bar{n} - 1) - \frac{J}{2} \sum_{\sigma} \bar{n}_{\sigma}(1 - \bar{n}_{\sigma}) , \quad (45)$$

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

$$\eta_{c,c;\sigma}^{\text{dc}} = - [U(\bar{n} - 1/2) + J(\bar{n}_{\sigma} - 1/2)] . \quad (46)$$

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

Translational invariant lattice systems

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 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.

Translational invariant lattice systems

Further simplifications for 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 nickel atoms. Then, U and J determine the atomic spectrum completely.
- In cubic symmetry, some matrices become diagonal

$$q_{c,\sigma}^{c',\sigma} = \delta_{c,c'} (\delta_{c,t_{2g}} q_{t,\sigma} + \delta_{c,e_g} q_{e,\sigma}) , \quad (47)$$

$$\rho_{(\mathbf{R},b'),(\mathbf{R},b); \sigma}^G = \delta_{b,b'} \rho_{(\mathbf{R},b),(\mathbf{R},b); \sigma} . \quad (48)$$

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

Translational invariant lattice systems

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 (`Wannier90` not yet implemented).

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 density-density interactions only requires smaller Coulomb parameters;
- The choice of the double-counting corrections.

Translational invariant lattice systems

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

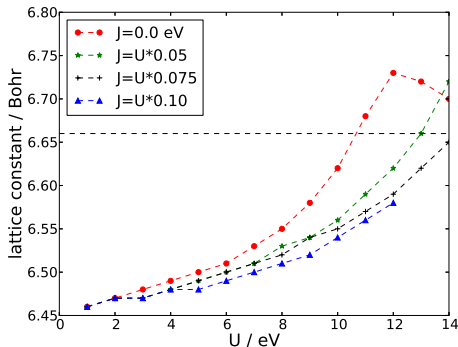


Fig. 1: fcc lattice constant of nickel as a function of U for different values of J/U , calculated with the full local Hamiltonian $\hat{V}_{\text{loc}}^{\text{full}}$ and the LDA+ U double counting correction; dashed line: experimental value.

In DFT: the lattice constant is too small; the Gutzwiller approach resolves this problem if we choose $U > 10$ eV.

Translational invariant lattice systems

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

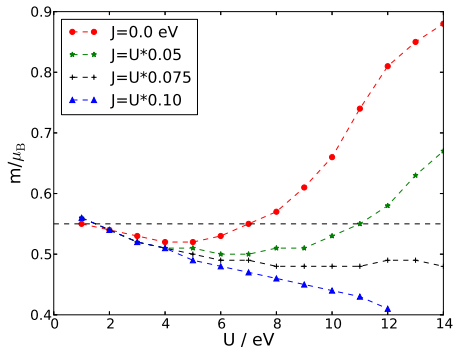


Fig. 2: magnetic moment of nickel as a function of U for different values of J/U , calculated with the full local Hamiltonian \hat{V}_{loc}^{full} and the LDA+ U double counting correction; dashed line: experimental value.

If we choose $U_{opt} = 13 \text{ eV}$ and $J_{opt} = 0.9 \text{ eV}$ ($J/U = 0.7$), we obtain a good agreement with the experimental values for a and m .

Translational invariant lattice systems

For $U_{\text{opt}} = 13 \text{ eV}$ and $J_{\text{opt}} = 0.9 \text{ eV}$ ($J/U = 0.7$), we calculate the bulk modulus.

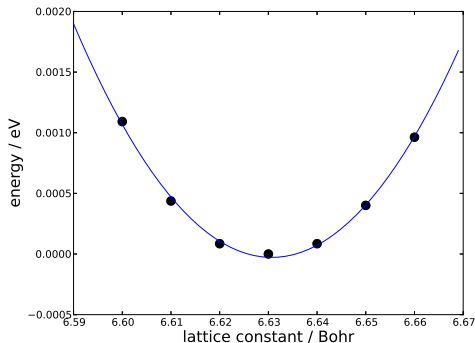


Fig. 3: Ground-state energy per particle $E_0(a)/N$ relative to its value at $a = 6.63a_B$ as a function of the fcc lattice parameter a/a_B , calculated with the full local Hamiltonian $\hat{V}_{\text{loc}}^{\text{full}}$ and the LDA+ U double counting correction; full line: 2nd-order polynomial fit.

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

Translational invariant lattice systems

For $U_{\text{opt}} = 13 \text{ eV}$ and $J_{\text{opt}} = 0.9 \text{ eV}$ ($J/U = 0.7$), we derive the quasi-particle band structure.

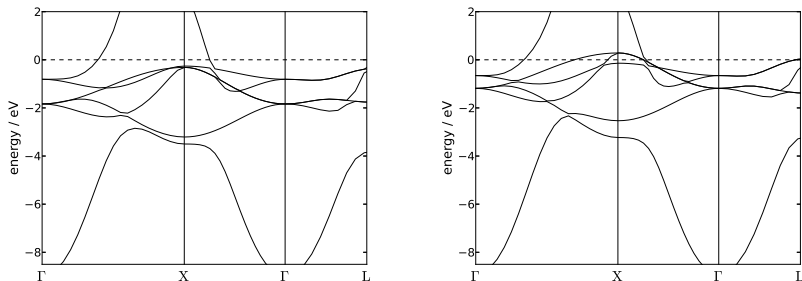


Fig. 4: quasi-particle band structure of fcc nickel along high-symmetry lines in the first Brillouin zone, calculated with the full local Hamiltonian $\hat{V}_{\text{loc}}^{\text{full}}$ and the LDA+ U double counting correction; left: majority spin; right: minority spin; Fermi energy $E_{\text{F}}^{\text{G}} = 0$.

Translational invariant lattice systems

Symmetry	Experiment	\hat{V}_{loc}^{full}	\hat{V}_{loc}^{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).

$\langle \dots \rangle$ 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.

Translational invariant lattice systems

Improvements

- Gutzwiller-DFT gets the correct $3d$ bandwidth ($W_{G-DFT} = 3.3 \text{ eV}$, whereas $W_{DFT} = 4.5 \text{ eV}$).
- Gutzwiller-DFT gets the correct Fermi-surface topology (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).

Conclusions

Summary

- Formalism:
 - We presented a formal derivation of the Gutzwiller Density Functional Theory.
 - 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 are proven to be correct.
- Results for nickel:
 - Experimental values for the lattice constant, the bulk modulus and the magnetic moment are reproduced for $U = 13 \text{ eV}$ and $J = 0.9 \text{ eV}$.
 - The band width, the Fermi surface topology, and the overall band structure reproduce the experimental data fairly well.
 - No fine tuning of parameters is required.

Conclusions

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.
- Well localized correlated orbitals must be constructed & used.
- The double-counting problem must be solved in a canonical way; ad-hoc potentials are not helpful in the long run.