The Gutzwiller variational theory: Electronic and magnetic properties of transition metals

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Outline: I) Introduction

II) Generalised Gutzwiller theory

III) Ferromagnetism in a two-band Hubbard model

IV) Model systems for transition metals

V) Nickel

VI) Iron

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I) Introduction

Consider: one-band Hubbard model:

$$\hat{H} = \sum_{i,j,\sigma} t_{i,j} \hat{c}^{\dagger}_{i,\sigma} \hat{c}_{j,\sigma} + \sum_{i} U \hat{n}_{i,\uparrow} \hat{n}_{i,\downarrow}$$

Gutzwiller variational wave function (1963):

$$|\Psi_{\mathrm{G}}\rangle = \hat{P} |\Phi_0\rangle$$

with

$$\hat{P}_{\mathrm{G}} = \prod_{i} \hat{P}_{\mathrm{G},i}$$

$|\Phi_0\rangle$: one-particle wave function (Slater-determinant)

Gutzwiller-correlator: $\hat{P}_{\mathrm{G},i} = \sum_{\Gamma} \lambda_{\Gamma} |\Gamma\rangle_i \langle\Gamma|_i$

with variational parameters λ_{Γ}

and 'atomic' eigenstates: $|\emptyset\rangle = |\mathrm{vac}\rangle$, $|d\rangle_i = \hat{c}^\dagger_{i,\uparrow}\hat{c}^\dagger_{i,\downarrow}|\mathrm{vac}\rangle$,

$|\uparrow\rangle_i = \hat{c}^\dagger_{i,\uparrow}|\mathrm{vac}\rangle$, $|\downarrow\rangle_i = \hat{c}^\dagger_{i,\downarrow}|\mathrm{vac}\rangle$

Problem: $|\Psi_G\rangle$ is still a many-particle wave-function

→ evaluation of $E_{\mathrm{var}} = \dfrac{\langle \Psi_{\mathrm{G}}|\hat{H}|\Psi_{\mathrm{G}}\rangle}{\langle \Psi_{\mathrm{G}}|\Psi_{\mathrm{G}}\rangle}$

in general not possible

Approximate Solution: { Gutzwiller approximation $\hat{=}$ Limit of infinite spatial dimensions

Gutzwiller approximation:

$$E_{\rm var} = \sum_{i,j,\sigma} q_\sigma^2 t_{i,j} \langle \hat{c}^\dagger_{i\sigma} \hat{c}_{j,\sigma} \rangle_{\Phi_0} + U \sum_i \lambda_d^2 \underbrace{(n_{\uparrow,0} n_{\downarrow,0})}_{= \langle \hat{n}_{i,\uparrow} \hat{n}_{i,\downarrow} \rangle_{\Phi_0}}$$

with renormalisation factors

$$q_\uparrow = \lambda_\emptyset \lambda_\uparrow (1 - n_{\downarrow,0}) + \lambda_d \lambda_\downarrow (n_{\downarrow,0}) \qquad (n_{\sigma,0} = \langle \hat{n}_\sigma \rangle_{\Phi_0})$$

Generalised Gutzwiller theory

Multi-band Hubbard models:

$$\hat{H} = \sum_{i\neq j;\sigma,\sigma'} t_{i,j}^{\sigma,\sigma'} \hat{c}_{i,\sigma}^{\dagger} \hat{c}_{j,\sigma'} + \sum_{i} \hat{H}_{\mathrm{loc},i} = \hat{H}_0 + \hat{H}_{\mathrm{loc}}$$

with local 'atomic' Hamiltonian (index i skipped):

$$\hat{H}_{\mathrm{loc},i} = \sum_{\sigma_1,\sigma_2,\sigma_3,\sigma_4} U_{\sigma_1,\sigma_2,\sigma_3,\sigma_4} \hat{c}_{\sigma_1}^{\dagger} \hat{c}_{\sigma_2}^{\dagger} \hat{c}_{\sigma_3} \hat{c}_{\sigma_4} + \sum_{\sigma_1,\sigma_2} \varepsilon_{\sigma_1,\sigma_2} \hat{c}_{\sigma_1}^{\dagger} \hat{c}_{\sigma_2}$$

$$= \sum_{\Gamma} E_{\Gamma} |\Gamma\rangle\langle\Gamma|$$

σ : combined spin-orbital index

$|\Gamma\rangle$: atomic eigenstates with energies E_{Γ}

(assumed to be known, at least numerically) generalised Gutzwiller wave functions:

$$|\Psi_{\rm G}\rangle = \hat{P}|\Phi_0\rangle \quad , \quad \hat{P}_{\rm G} = \prod_i \hat{P}_{{\rm G},i}$$

$|\Phi_0\rangle$: one-particle wave function

with

$$\hat{P}_{{\rm G},i} = \sum_{\Gamma,\Gamma'} \lambda_{\Gamma,\Gamma'} |\Gamma\rangle_i \langle\Gamma'|_i$$ ($\lambda_{\Gamma,\Gamma'}$: variational parameters)

evaluation in infinite dimensions:

$$E_{\rm loc} = L \sum_{\Gamma} E_{\Gamma} m_{\Gamma} \qquad (m_{\Gamma} \equiv \langle \hat{m}_{\Gamma} \rangle_{\Psi_{\rm G}})$$

$$E_0 = \sum_{i \neq j} \sum_{\gamma,\gamma'} \underbrace{\sum_{\sigma,\sigma'} Q^{\gamma,\gamma'}_{\sigma,\sigma'} t^{\sigma,\sigma'}_{i,j}}_{\equiv \tilde{t}^{\gamma,\gamma'}_{i,j}} \langle \hat{c}^{\dagger}_{i,\gamma} \hat{c}_{i,\gamma'} \rangle_{\Phi_0}$$

(effective hopping)

m_Γ and $Q^{\gamma,\gamma'}_{\sigma,\sigma'}$ are functions of $\lambda_{\Gamma,\Gamma'}$

and of the local density matrix $C^0_{\sigma,\sigma'} = \langle \hat{c}^\dagger_{i,\sigma} \hat{c}_{i,\sigma'} \rangle_{\Phi_0}$

minimisation with respect to $|\Phi_0\rangle$:

→ effective one-particle Schrödinger equation for $|\Phi_0\rangle$:

$$\hat{H}^{\text{eff}}_0 |\Phi_0\rangle = E^{\text{eff}}_0 |\Phi_0\rangle$$

$$\hat{H}^{\text{eff}}_0 = \sum_{i \neq j} \sum_{\sigma,\sigma'} \tilde{t}^{\sigma,\sigma'}_{i,j} \hat{c}^\dagger_{i,\sigma} \hat{c}_{j,\sigma'} + \sum_i \sum_{\sigma,\sigma'} \eta_{\sigma,\sigma'} \hat{c}^\dagger_{i,\sigma} \hat{c}_{j,\sigma'}$$

Lagragne multipliers $\eta_{\sigma,\sigma'}$ determine density matrix $C^0_{\sigma,\sigma'}$

Diagonalisation: $\hat{H}^{\text{eff}}_0 = \sum_{k,\gamma} E_{k,\gamma} \hat{h}^\dagger_{k,\gamma} \hat{h}_{k,\gamma}$, $|\Phi_0\rangle = \prod_{\substack{k,\gamma \\ (E_{k,\gamma} < E_{\text{F}})}} \hat{h}^\dagger |0\rangle$

→ remaining variational parameters: $\lambda_{\Gamma,\Gamma'}$ and $\eta_{\sigma,\sigma'}$

Remaining problems:

i) Number of variational parameters, e.g. 3d-shell:

if $\lambda_{\Gamma,\Gamma'}$ finite for all Γ,Γ' with the same particle number

→ $\approx 2\cdot 10^5$ variational parameters

solution: finite coupling only for 'relevant' Γ,Γ'

e.g. $\lambda_{\Gamma,\Gamma'}\sim\delta_{\Gamma,\Gamma'}$

ii) How to compare to experiments?

Landau-Fermi liquid theory: quasi-particle energies $E_{k,\tau}$

from $$\hat{H}_0^{\text{eff}}=\sum_{k,\gamma}E_{k,\gamma}\hat{h}^{\dagger}_{k,\gamma}\hat{h}_{k,\gamma}$$

$$=\sum_{i\neq j}\sum_{\sigma,\sigma'}\tilde{t}^{\sigma,\sigma'}_{i,j}\hat{c}^{\dagger}_{i,\sigma}\hat{c}_{j,\sigma'}+\sum_{i}\sum_{\sigma,\sigma'}\eta_{\sigma,\sigma'}\hat{c}^{\dagger}_{i,\sigma}\hat{c}_{j,\sigma'}$$

III) Ferromagnetism in a two-band model

Local Hamiltonian:

$$\hat{H}_{\text{loc}} = U \sum_b \hat{n}_{b,\uparrow}\hat{n}_{b,\downarrow} + U' \sum_{\sigma,\sigma'} \hat{n}_{1,\sigma}\hat{n}_{2,\sigma'} - J \sum_{\sigma} \hat{n}_{1,\sigma}\hat{n}_{2,\sigma}$$
$$+ J \sum_{\sigma} \hat{c}^{\dagger}_{1,\sigma}\hat{c}^{\dagger}_{2,-\sigma}\hat{c}_{1,-\sigma}\hat{c}_{2,\sigma} + J_C \left(\hat{c}^{\dagger}_{1,\uparrow}\hat{c}^{\dagger}_{1,\downarrow}\hat{c}_{2,\downarrow}\hat{c}_{2,\uparrow} + \text{h.c.} \right)$$

e_{g} -orbitals: $J = J_C$ and $U - U' = 2J$

two-particle states:

states	energy	symmetry
$\lvert\uparrow,\uparrow\rangle$ $\left(\lvert\uparrow,\downarrow\rangle + \lvert\downarrow,\uparrow\rangle\right)/\sqrt{2}$ $\lvert\downarrow,\downarrow\rangle$	$U - 3J$	$^3A_2$
$\left(\lvert\uparrow,\downarrow\rangle - \lvert\downarrow,\uparrow\rangle\right)/\sqrt{2}$ $\left(\lvert\uparrow\downarrow,0\rangle - \lvert 0,\downarrow\uparrow\rangle\right)/\sqrt{2}$	$U - J$	^1E
$\left(\lvert\uparrow\downarrow,0\rangle + \lvert 0,\downarrow\uparrow\rangle\right)/\sqrt{2}$	$U + J$	$^1A_1$

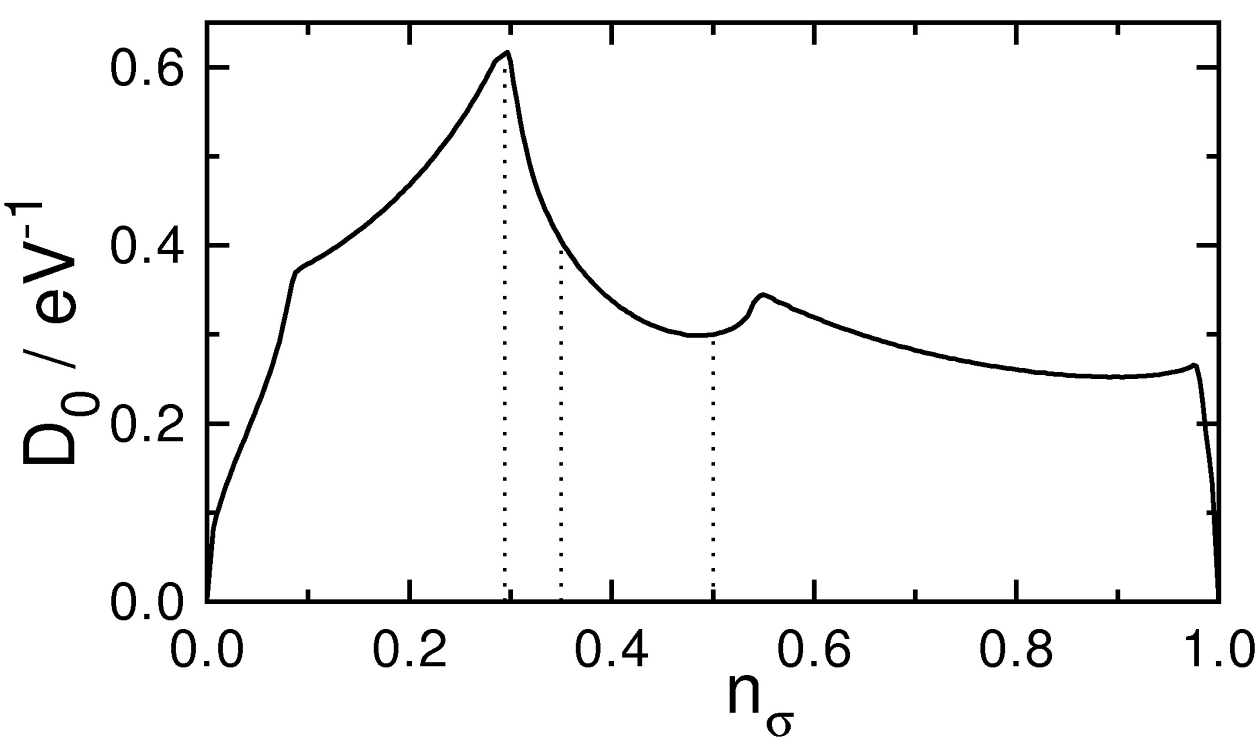
Gutzwiller wave-function: i) no multiplet coupling

$$\lambda_{\Gamma,\Gamma'} \sim \delta_{\Gamma,\Gamma'}$$

$|\Gamma\rangle$: atomic eigenstates

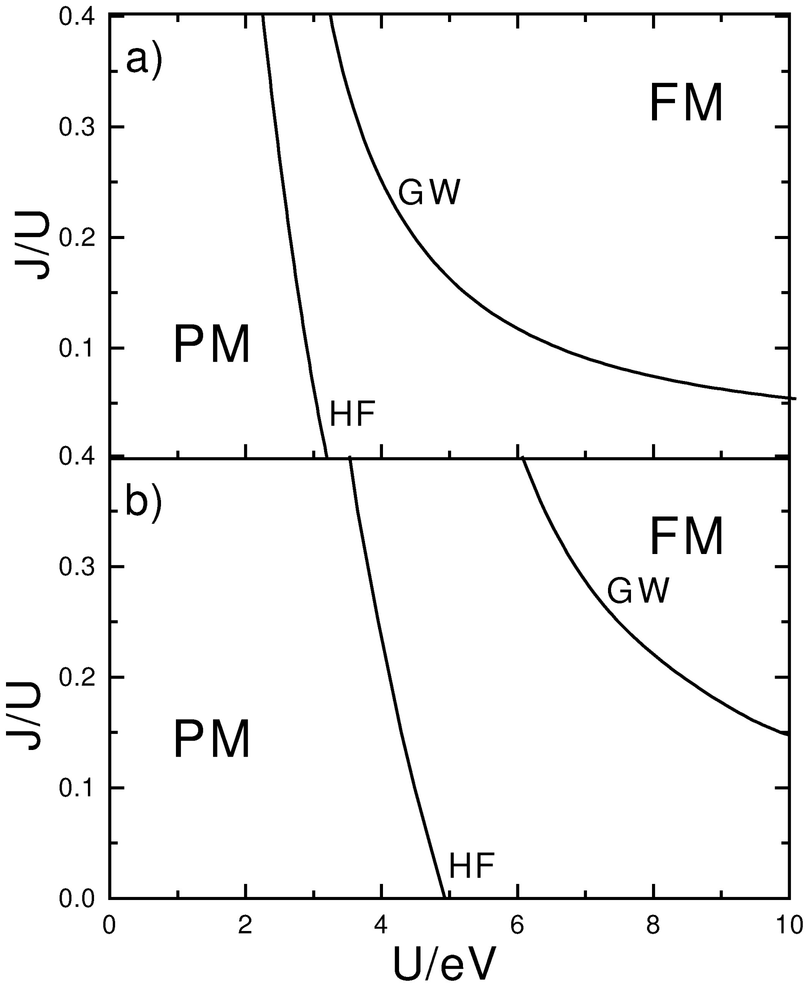
ii) $|\Phi_0\rangle$: spin-polarised Fermi-sea

density of states:

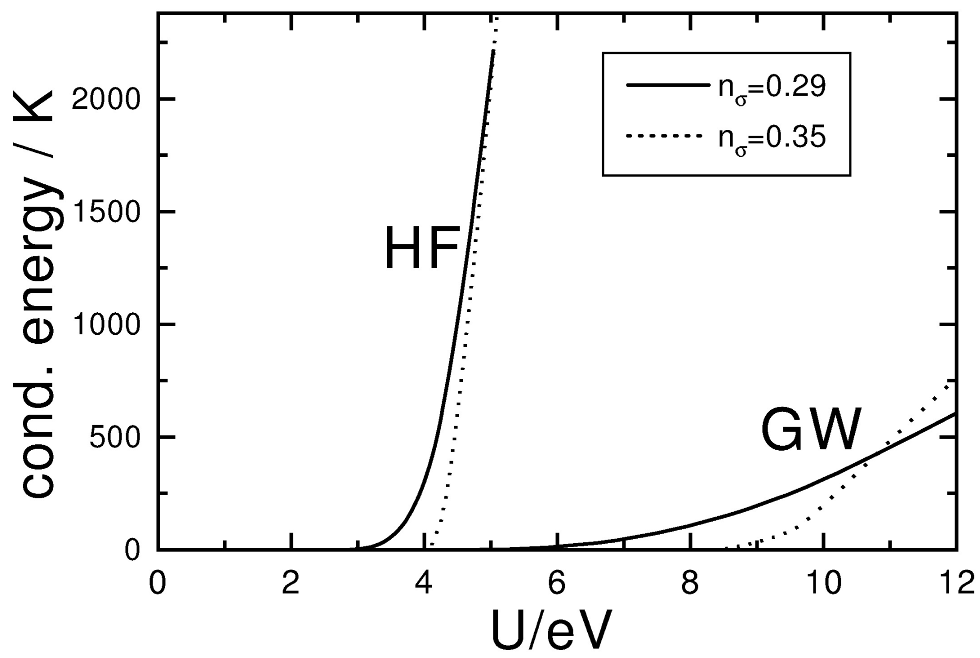


Results:

phase-diagram



condensation-energy



IV) Transition metals: model systems

i) $\hat{H}_0$: from tight-binding fits to the paramagnetic DFT band-structures (4s,4p,3d-orbitals)

ii) $\hat{H}_{\rm loc}$:

- onsite energy $\varepsilon_{\sigma,\sigma}$ (from tight-binding fits)
- Coulomb-interaction: spherical approximation

→ Racah parameters:

$A = 8 - 9\mathrm{eV}$ (from 3d band-width)

$B \approx 0.1\mathrm{eV}$, $C \approx 0.4\mathrm{eV}$ (from atom physics)

iii) local spin-orbit coupling $\hat{H}_{\rm SO} = \frac{\zeta}{2} \sum_{\sigma,\sigma'} \langle \sigma | \hat{\vec{l}} \cdot \hat{\vec{s}} | \sigma' \rangle \hat{c}^{\dagger}_{\sigma} \hat{c}_{\sigma'}$

$\zeta \approx 0.08\mathrm{eV}$ (from atom physics)

V) fcc-Nickel

Comparison: ARPES (exp) ⟷ SDFT

i) width of d-bands: $W \approx 3.3\text{eV}$ (exp)

$W \approx 4.5\text{eV}$ (SDFT)

→ experimental band-structure not reproduced

ii) exchange splitting of $\uparrow - \downarrow$ bands:

(SDFT)	(exp)
$\Delta \approx 0.7\text{eV}$	$\Delta \approx 0.16\text{eV}\ (e_{\mathrm{g}})$
(isotropic)	$\Delta \approx 0.33\text{eV}\ (t_{2\mathrm{g}})$

iii) Topology of the Fermi-surface around the X-point:

(SDFT) $X_{2\downarrow}(e_{\mathrm{g}})$ $X_{5\downarrow}(t_{2\mathrm{g}})$ above E_{F} → 2 hole-ellipsoids

(Exp) $X_{2\downarrow}(e_{\mathrm{g}})$ below E_{F}, $X_{5\downarrow}(t_{2\mathrm{g}})$ above E_{F} → 1 hole-ellipsoids

Results of the Gutzwiller theory (without spin-orbit coupling)

i) d-band width: $3.3\mathrm{eV}$ (correct by construction)

ii) Exchange splitting:

$\Delta \approx 0.13\mathrm{eV}$ (e_{g}) (exp: $0.16\mathrm{eV}$)

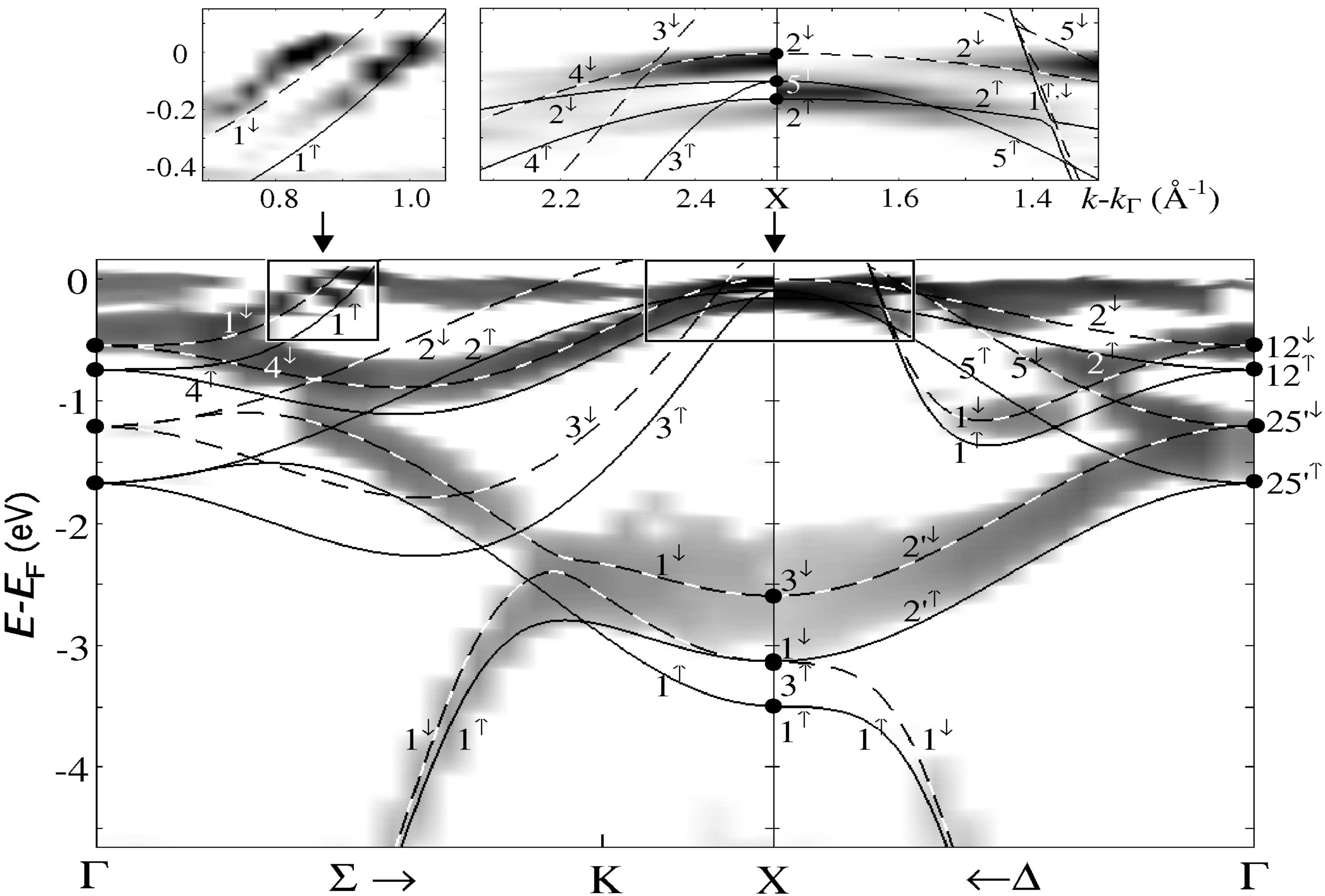
$\Delta \approx 0.29\mathrm{eV}$ $(t_{2\mathrm{g}})$ (exp: $0.33\mathrm{eV}$)

iii) Correct Fermi-surface topology around the X-point:

$$E(X_{2\downarrow}) - E_{\mathrm{F}} \approx -0.02\mathrm{eV} < 0$$

iv) Correct quasi-particle bands

Comparison: ARPES ←→ Gutzwiller-theory



Spin-orbit coupling in fcc-Nickel

i) orbital moment: $\mu_{\rm orb} \approx 0.05\mu_{\rm B}$

(compare: $\mu_{\rm spin} \approx 0.5\mu_{\rm B}$)

ii) magnetic anisotropy:

$$E(111) - E(001) \approx -3\mu{\rm eV} < 0$$ (exp/GW)

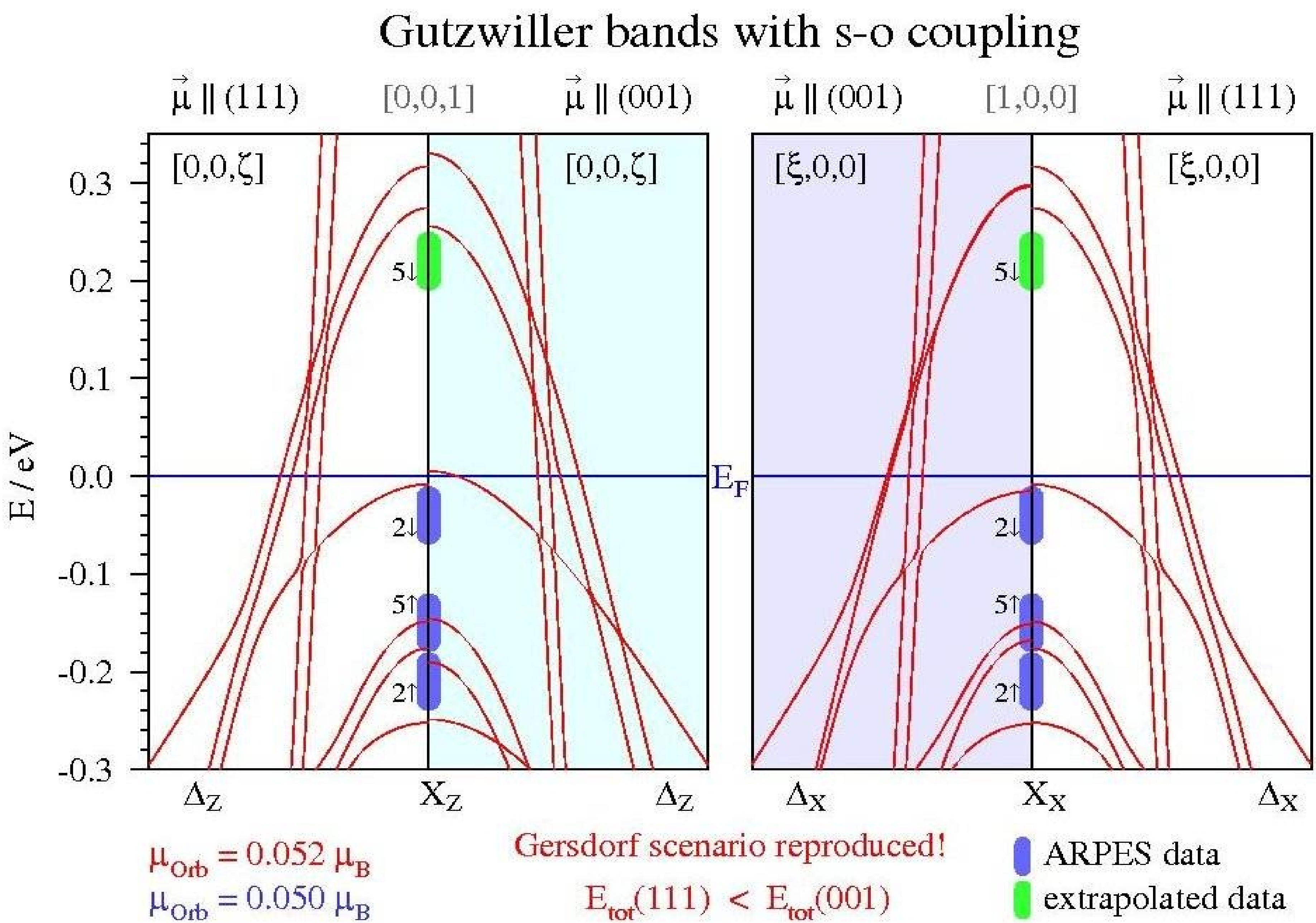
$\rightarrow$ $\vec{\mu}||(111)$

> 0 (in SDFT)

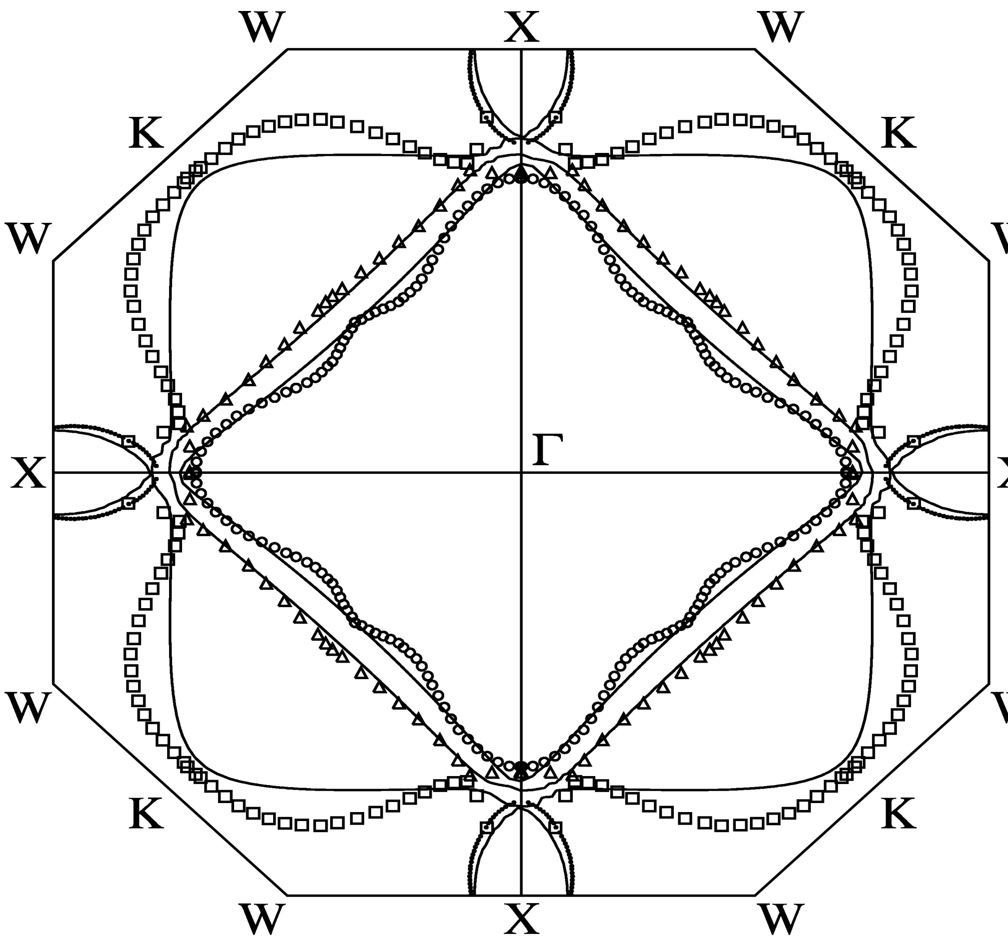
iii) 'Gersdorf effect':

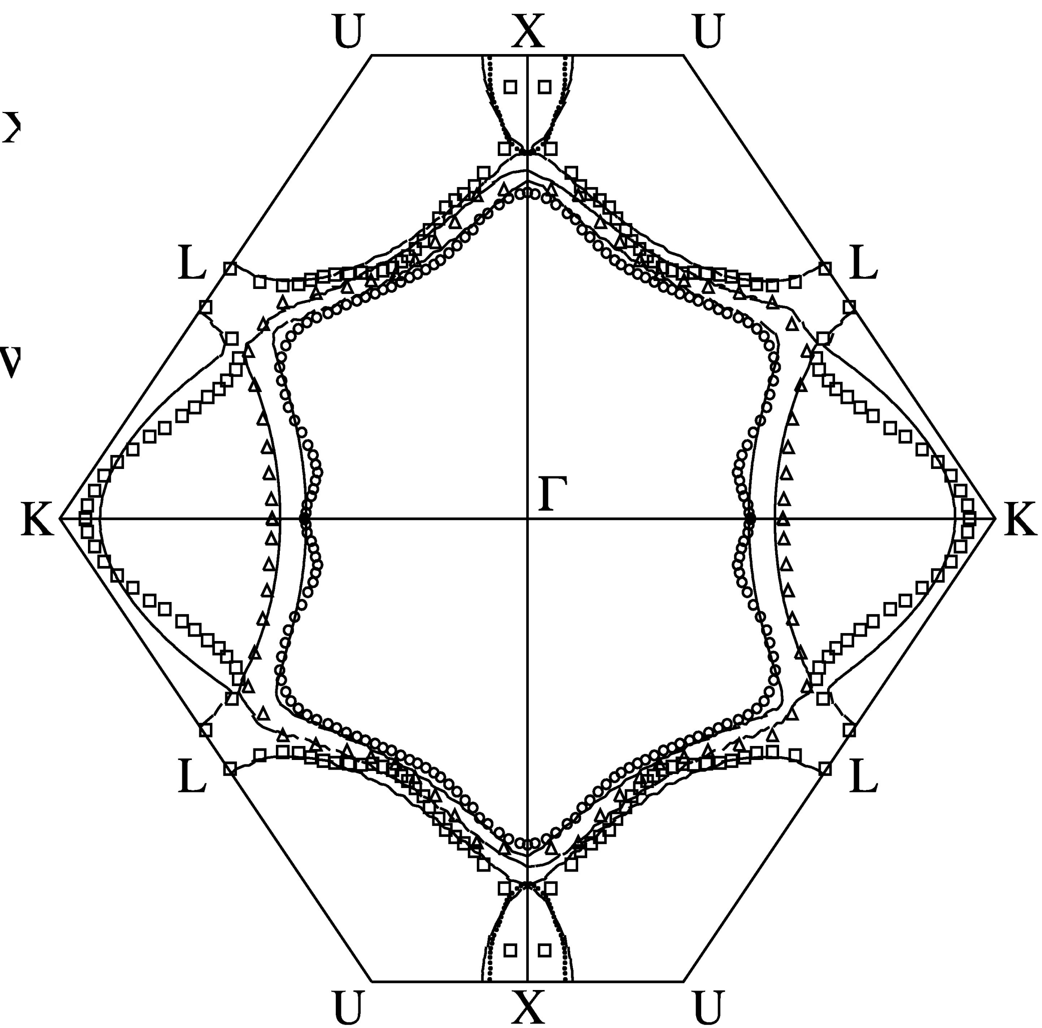
One of the states $X_{2\downarrow}$ moves above $E_{\rm F}$ if the magnetic moment direction is changed by a magnetic field

Gersdorf effect:



Fermi-surface:





VI) bcc-Iron

Comparison: Experiment ⟷ SDFT

i) width of d-bands: $W \approx 3.8\text{eV}$ (exp)

$W \approx 4.5\text{eV}$ (SDFT)

→ experimental band-structure not well reproduced

ii) exchange splitting of $\uparrow - \downarrow$ bands:

strong energy and orbital dependence:

$\Delta \approx 0.9 - 2.1\text{eV}$ from lowest-highest d-bands

iii) orbital moment: $\mu_{\text{orb}} \approx 0.1\mu_{\text{B}}$ $(\mu_{\text{spin}} \approx 2.1\mu_{\text{B}})$

iv) magnetic anisotropy:

$E(111) - E(001) \approx 1.5\mu\text{eV} > 0$ → $\vec{\mu}||(001)$

Problems and first results

i) magnetic anisotropy:

with diagonal variational parameters $(\lambda_{\Gamma,\Gamma'} \sim \delta_{\Gamma,\Gamma'})$

→ Nickel: correct results

→ mixing of states is not important

But for Iron:

anisotropy energy 3 orders of magnitude too large !

→ the atomic states must be determined variationally

$$\hat{P}_{\mathrm{G}} = \sum_{\tilde{\Gamma}} \lambda_{\tilde{\Gamma}} |\tilde{\Gamma}\rangle\langle\tilde{\Gamma}| \hat{=} \sum_{\Gamma,\Gamma'} \lambda_{\Gamma,\Gamma'} |\Gamma\rangle\langle\Gamma'|$$

first numerical implementation:

finite $\lambda_{\Gamma,\Gamma'}$ for all Γ, Γ' of the same spherical multiplet

→ correct sign and order of magnitude of the anisotropy energy

ii) Energy dependence of the exchange splitting

cannot be explained without 4d-orbitals in the Hamiltonian

reason: large exchange-splitting in Iron

→ majority and minority bands hybridize differently with 4d-bands

→ increasing exchange-splitting from the bottom to to the top of the 3d-bands

Summary and Outlook

1) The Gutzwiller variational theory is a promising new tool for the investigation of real correlated electron systems

2) Further studies on Iron and other transition metals will be needed to assess the quality of the approach

3) A time-dependent Gutzwiller theory is available for the one-band Hubbard model (Götz Seibold et al.)

→ work on multi-band models will start soon

Landau-Gutzwiller quasi-particles

There is a one-to-one correspondence of excitations

in a Fermi-liquid and those in a Fermi-gas

Mathematically: there are operators $\hat{e}^{\dagger}_{k,\tau}$ and $\hat{v}_{k,\tau}$

with $\hat{e}^{\dagger}_{k,\tau}\hat{v}_{k,\tau}|\Psi_{\mathrm{G}}\rangle = \Theta(E_{\mathrm{F}} - E_{k,\tau})|\Psi_{\mathrm{G}}\rangle$

(i.e., Fermi-gas momentum distribution)

one finds Fermi operators:

$$\hat{e}^{\dagger}_{k,\tau} = \hat{P}_{\mathrm{G}}\hat{h}^{\dagger}_{k,\tau}(\hat{P}_{\mathrm{G}})^{-1}$$

$$\hat{v}_{k,\tau} = \hat{P}_{\mathrm{G}}\hat{h}_{k,\tau}(\hat{P}_{\mathrm{G}})^{-1}$$

quasi-particle/hole states

$$|\Psi_{\mathrm{G},+}^{(k,\tau)}\rangle \equiv \hat{e}_{k,\tau}^{\dagger}|\Psi_{\mathrm{G}}\rangle = \hat{P}_{\mathrm{G}}\hat{h}_{k,\tau}^{\dagger}|\Psi_0\rangle$$

$$|\Psi_{\mathrm{G},-}^{(k,\tau)}\rangle \equiv \hat{v}_{k,\tau}^{\dagger}|\Psi_{\mathrm{G}}\rangle = \hat{P}_{\mathrm{G}}\hat{h}_{k,\tau}|\Psi_0\rangle$$

quasi-particle energy-bands:

$$E_{\pm}^{\mathrm{var}}(k,\tau) = \frac{\langle\Psi_{\mathrm{G},\pm}^{(k,\tau)}|\hat{H}|\Psi_{\mathrm{G},\pm}^{(k,\tau)}\rangle}{\langle\Psi_{\mathrm{G},\pm}^{(k,\tau)}|\Psi_{\mathrm{G},\pm}^{(k,\tau)}\rangle} - E_{\mathrm{var}} = E_{k,\tau}$$

with $E_{k,\tau}$ eigenvalues of $\hat{H}_0^{\mathrm{eff}} = \sum_{k,\gamma} E_{k,\gamma}\hat{h}_{k,\gamma}^{\dagger}\hat{h}_{k,\gamma}$

$$\hat{H}_0^{\mathrm{eff}} = \sum_{i\neq j}\sum_{\sigma,\sigma'}\tilde{t}_{i,j}^{\sigma,\sigma'}\hat{c}_{i,\sigma}^{\dagger}\hat{c}_{j,\sigma'} + \sum_{i}\sum_{\sigma,\sigma'}\eta_{\sigma,\sigma'}\hat{c}_{i,\sigma}^{\dagger}\hat{c}_{j,\sigma'}$$

Brinkman-Rice transition at half filling

$$E_{\rm var} = 2\left(2-\lambda_d^2\right)\lambda_d^2\varepsilon_0 + U\lambda_d^2\frac{1}{4}$$

with $\quad \varepsilon_0 = \sum_{i,j} t_{i,j}\langle \hat{c}^\dagger_{i\sigma}\hat{c}_{j,\sigma}\rangle_{\Phi_0}$

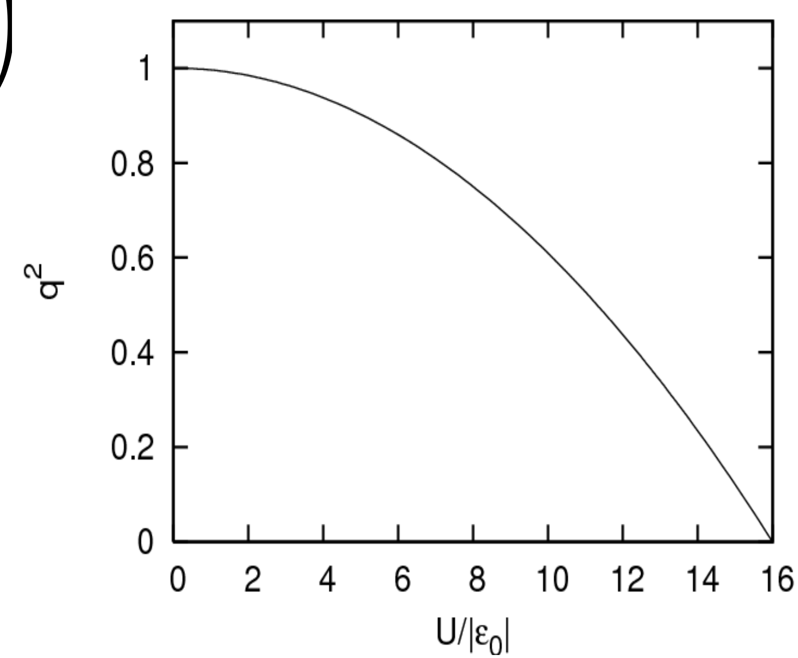
minimisation: $\quad q_\sigma^2 = 1-\left(\frac{U}{U_c}\right)^2 \qquad (U_c = 16|\varepsilon_0|)$

$$\langle\hat{d}\rangle = \frac{1}{4}\left(1-\left(\frac{U}{U_c}\right)\right)$$

effective mass: $\quad m^* \sim 1/q \to \infty$

$$\uparrow$$

$$(U \to U_c)$$



Gutzwiller approximation:

$$E_{\rm var} = \sum_{i,j,\sigma} q_\sigma^2 t_{i,j} \langle \hat{c}_{i\sigma}^\dagger \hat{c}_{j,\sigma} \rangle_{\Phi_0} + U \sum_i \lambda_d^2 (n_{\uparrow,0} n_{\downarrow,0})$$

with renormalisation factors

$$q_\uparrow = \lambda_\emptyset \lambda_\uparrow (1 - n_{\downarrow,0}) + \lambda_d \lambda_\downarrow (n_{\downarrow,0}) \qquad (n_{\sigma,0} = \langle \hat{n}_\sigma \rangle_{\Phi_0})$$

constraints i) $1 = \sum_\Gamma \langle \hat{m}_\Gamma \rangle_{\Psi_{\rm G}} \qquad (\hat{m}_\Gamma \equiv |\Gamma\rangle\langle\Gamma|)$

ii) $n_{\sigma,0} = \langle \hat{n}_\sigma \rangle_{\Psi_{\rm G}}$

determine three of the four parameters λ_Γ

e.g. half filling $n_{\sigma,0} = \dfrac{1}{2}$

→ Mott-transition