Multi-Band Gutzwiller Method Based on DFT: Application to Ni

1. Introduction
   Localized vs itinerant moments
2. The Multi-band Gutzwiller scheme
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magnetic insulators:

Localized spins
strong on-site e-e interaction

multiplet structure of 3d ions
somewhat modified by ligand fields
Hund's rules are valid

metallic ferromagnets:

itinerant d-electrons, Spins
moderately strong e-e interaction (screening by s-electrons)

band theory works well
Fermi surfaces, moments, Photoemission

implies: multiplets vanished
Hund's rules unimportant

Itinerant vs Localized

Stoner
Wohlfahrt
Slater

weak e-e interaction

one-particle picture prevails

↳ non-integer moments

van Vleck

strong e-e i.

charge fluctuations strongly suppressed

atomic-like moments

reduced itinerancy

HF

⋮

SDFT

Hubbard Model

Hubbard I, II, III

Gutzwiller

$\varepsilon_k \rightarrow q\varepsilon_k$

$0 \leq q \leq 1$

FL, M-I transition

DFT ◯◯ Multiband Gutzwiller

Similar attempts: LDA + U, LDA ++, HF, Hubbard I

metallic ferromagnetism:

Spin-Density-Functional theory

Slater (1953): averaged exchange pot. $\bar{v}_x$ for 1-particle energy bands

Kohn, Hohenberg (1968): ground state is functional of charge density ϱ (and of spin density $\vec{m}$)

Kohn Sham (1968): effective 1-particle equations for ϱ using

$v_{xc} = v_{xc}[\varrho]$ local density approx using results of electron gas theory

Hedin, Lundqvist et al. 1971...: generalization to SDFT

$v_{xc} \rightarrow v_{xc}[\varrho, \vec{m}]$

1975... highly accurate numerical methods (LAPW, KKR, NC PP)

good agreement with exp.

Hartree-Fock approx. for metals:

enormous charge fluctuations

example: degenerate 2-band model, half filled

occupancy	□	1	2	3	4
probability (statistical)	$\frac{1}{16}$	$\frac{4}{16}$	$\frac{6}{16}$	$\frac{4}{16}$	$\frac{1}{16}$

$\bar{N} = 2 = 0 + \frac{1}{4} + \frac{3}{4} + \frac{3}{4} + \frac{1}{4}$

metallic behavior in the limit of strong correlations:

$[2] \lesssim 1 \qquad [1], [3] \ll 1$

$[\,], [4] = 0$

"minimum polarity" model of van Vleck 1953

⇒ **Gutzwiller method**
variationally modifies
atomic multiple occupancies

Gutzwiller variational wave function

applied for Hubbard model 1963

double occupancy of sites is variational parameter

- fulfills Luttingers theorem
- metal-insulator transition (Brinkman-Rice)
- metallic case:
  Fermi liquid description of electrons

↪ effective single particle bands

$\tilde{\varepsilon}_k = q\,\varepsilon_k^{bare}$

$0 \leq q \leq 1$

$q \propto \frac{1}{\left(\frac{m_{eff}}{m_0}\right)}$

insulator through localisation of electrons

no e-e interaction

One-Band case (Hubbard Model)

$$\hat{H} = \sum_{ij\sigma} t_{ij}\, \hat{c}^{+}_{i\sigma}\, \hat{c}_{j\sigma} + \frac{1}{2} U \sum_{i\sigma} \hat{n}_{i\sigma}\, n_{i\bar{\sigma}}$$

Gutzwiller WF: $|\Psi_{GW}\rangle = \hat{P}_i\, |\Psi_0(\Delta_{ex})\rangle$

correlator: $\hat{P}_i = 1 + (\lambda_i - 1)\, \hat{n}_{i\sigma}\, \hat{n}_{i\bar{\sigma}}$

λ_i: variational parameter ⇐ $\hat{P}_i$ projection op.

↑↓	12	m_{12}
↑	1	$m_\uparrow$; $n_\uparrow = m_\uparrow + m_{12}$
↓	2	$m_\downarrow$ $n_\downarrow = m_\downarrow + m_{12}$
—	0	m_σ $1 = m_\sigma + m_\uparrow + m_\downarrow + m_{12}$

Ground state energy (Gutzwiller approximation, periodic lattice)

$$E(m_{12}, \Delta_{ex}) = \sum_\sigma q_\sigma\, \bar{\varepsilon}_\sigma + m_{12} U$$

hopping reduction

$$q_\sigma = \frac{1}{n_\sigma(1-n_\sigma)} \left(\sqrt{m_\sigma m_\sigma} + \sqrt{m_{\bar{\sigma}} m_{12}}\right)^2$$

$\Rightarrow \sqrt{q_\sigma}\sqrt{q_{\sigma'}}$

$$\bar{\varepsilon}_\sigma = \sum_{k \in k_F^{(\sigma)}} \varepsilon_{k\sigma}$$

Multiband - Hamiltonian

$$\hat{H} = \sum_{\substack{ij \\ \beta\beta'}} t_{ij}^{\beta\beta'}\, \hat{c}^{+}_{i\beta}\, \hat{c}_{j\beta'} + \sum_i \hat{H}_{at;i}$$

β spin-orbital index

$$\hat{H}_{at} = \frac{1}{2} \sum_{\beta\beta'} U_{\beta\beta'}\, \hat{n}_\beta\, \hat{n}_{\beta'} + \frac{1}{2} \sum_{\beta_1\beta_2\beta_3\beta_4}{}' J_{\beta_1\beta_2\beta_3\beta_4}\, \hat{c}^{+}_{\beta_1} \hat{c}^{+}_{\beta_2} \hat{c}_{\beta_3} \hat{c}_{\beta_4}$$

minimum basis Hamiltonian to describe multiplet structure of open shell atoms

U, J: on-site Coulomb interaction

to be expressed by three Racah Parameters

$A \leftrightarrow U$ $\quad C/B \approx 4.5$

$B, C \Rightarrow J$ atomic exchange, Hund's rule I, II

Slater Integrals & Racah Parameters

(spherical symmetry)

Slater Integrals F^k $(k = 0, 2, 4)$

$$F^k(d_1, d_2) = \int_0^\infty r_1^2 dr_1 \int_0^\infty r_2^2 dr_2 \; R_{d_1}^2(r_1) \, R_{d_2}^2(r_2) \left(\frac{r_>}{r_<}\right)^k \cdot \frac{1}{r_<}$$

Slater - Condon Parameters

$$F_0 = F^0 \; ; \quad F_2 = \frac{1}{49} F^2 \; ; \quad F_4 = \frac{1}{441} F^4$$

Racah - Parameters

$$A = F_0 - 49 F_4 = F^0 - \frac{1}{9} F^4$$

$$B = F_2 - 5 F_4 = \frac{1}{49}\left(F^2 - \frac{5}{9} F^4\right)$$

$$C = 35 F_4 = \frac{5}{63} F^4$$

empirical: $4 \lesssim \frac{C}{B} \lesssim 5$ $C \approx 0.3\text{-}0.5$ eV

density - density interaction : $A + \beta B + \delta C$

exchange (spin, charge) : $\beta' B + \delta' C$

3-orb, 4-orb terms : $\beta'' B + \delta'' C$

multiband Gutzwiller method:

atomic n-electron basis states $|\Gamma\rangle$ ($|\uparrow\uparrow\rangle, |\uparrow\downarrow\rangle \ldots$)

" " eigen states $|\Gamma\rangle$

$$\hat{H}_{at} |\Gamma\rangle = E_\Gamma |\Gamma\rangle \; ; \quad |\Gamma\rangle = \sum_I T_{I,\Gamma} |I\rangle$$

↑ Condon-Shortley-Slater-Racah

matrix T nontrivial in general

projection operators:

$$\hat{m}_\Gamma = |\Gamma\rangle\langle\Gamma|$$

runs over all Γ of all n-electron configs

$N = 5 \Rightarrow 2^{2N}$

Gutzwiller wave function:

$$|\Psi_G\rangle = \prod_i \hat{P}_i \, |\Psi_0^{trial}\rangle$$

correlator for site i :

$$\hat{P}_i = 1 + \sum_\Gamma (\lambda_{i,\Gamma} - 1) \, \hat{m}_{i,\Gamma}$$

2^{2N} variational parameters $\lambda_{i,\Gamma} \langle = \rangle \langle \hat{m}_{i,\Gamma} \rangle$ per inequivalent site i

evaluated in the limit $D \to \infty$ for $\hat{H}_{at}^{dens}$

BGW J Phys CM 8, 7343 ('97)

Hasegawa, Frésard & Kotliar

multi-band Gutzwiller method:

$$E_{\text{ground state}} = \langle H \rangle = \frac{\langle \Psi_G | \hat{H} | \Psi_G \rangle}{\langle \Psi_G | \Psi_G \rangle}$$

$$= \sum_{\substack{ij \\ \sigma\sigma'}} \sqrt{q_{i\sigma}}\sqrt{q_{j\sigma'}}\, t_{ij}^{\sigma\sigma'} \langle \phi_0 | \hat{c}_{i\sigma}^{+} \hat{c}_{j\sigma'} | \phi_0 \rangle + \sum_{\Gamma} E_{\Gamma} m_{\Gamma}$$

$$\tilde{t}_{ij}^{\sigma\sigma'}$$

$$\sqrt{q_{\sigma}} = \sum_{\Gamma\Gamma'} S_{\Gamma\Gamma'} \sqrt{m_{\Gamma} m_{\Gamma'}}$$

m_{Γ} obey sum rules for orbital occ. n_{σ}

$$\langle \hat{H} \rangle = \langle \hat{H}_{\text{eff}} \rangle$$

$$\hat{H}_{\text{eff}} = \sum_{\substack{ij \\ \sigma\sigma'}} \tilde{t}_{ij}^{\sigma\sigma'} \hat{c}_{i\sigma}^{+} \hat{c}_{j\sigma'} + \sum_{\Gamma} E_{\Gamma} m_{\Gamma}$$

effective single particle Hamiltonian

$|\phi_0\rangle$ ground state of $\hat{H}_{\text{eff}}\{m_{\Gamma}\}$

to be determined self consistently

$|\phi_0\rangle \Rightarrow$ quasi particle bands $\tilde{\varepsilon}_{k\mu}$

most general case:

(low symmetry, large orbital basis)

e.g. spin-orbit coupling

$$\langle \hat{H} \rangle = \sum_{i \neq j;\sigma_1;\sigma_1'} \tilde{t}_{i,j}^{\sigma_1,\sigma_1'} \langle \hat{c}_{i;\sigma_1}^{+} \hat{c}_{j;\sigma_1'} \rangle_0 + \sum_{i;\sigma} \epsilon_{i;\sigma} n_{i;\sigma}$$

$$+ \sum_{i;\Gamma} E_{i;\Gamma} m_{i;\Gamma}, \qquad (21a)$$

$$\tilde{t}_{i,j}^{\sigma_1,\sigma_1'} = \sum_{\sigma_2,\sigma_2'} t_{i,j}^{\sigma_2,\sigma_2'} \sqrt{q_{i;\sigma_2}^{\sigma_1} q_{j;\sigma_2'}^{\sigma_1'}}. \qquad (21b)$$

$$\sqrt{q_\sigma^{\sigma'}} = \sqrt{\frac{1}{n_{\sigma'}^0(1-n_{\sigma'}^0)}} \sum_{\Gamma,\Gamma'} \sqrt{\frac{m_\Gamma m_{\Gamma'}}{m_\Gamma^0 m_{\Gamma'}^0}}$$

$$\times \sum_{\substack{l,l' \\ (\sigma \in l, \sigma' \notin l')}} \mathrm{fsgn}(\sigma', l')\,\mathrm{fsgn}(\sigma, l)$$

$$\times \sqrt{m^0_{(l'\cup\sigma')}} m^0_{l'} T^+_{\Gamma,(l\cup\sigma)} T_{(l'\cup\sigma'),\Gamma} T^+_{\Gamma',l'} T_{l,\Gamma'}, \qquad (22)$$

Iterative variational procedure

$$\hat{H}_{\mathrm{eff}}^{(0)} = \underbrace{\sum_{ij} t_{ij}^{\sigma\sigma'} \hat{c}_{i\sigma}^{+} \hat{c}_{j\sigma'} + \sum_{i\sigma} \varepsilon_i \hat{n}_{i\sigma}}_{\hat{H}_1} + \sum_{i\sigma} \Delta_{i\sigma} \hat{n}_{i\sigma}$$

"external" VP's $\Delta_{i\sigma}$ — exchange splitting (for each σ), crystal field splitting, shifts of orbital energies

$|\phi_0^{(0)}\{\Delta_{i\sigma}\}\rangle$ is ground state of $\hat{H}_{\mathrm{eff}}^{(0)}$

$$E_0^{(0)} = \sum_{\sigma\sigma'} \sqrt{q_\sigma\{m_\Gamma\}} \sqrt{q_{\sigma'}\{m_\Gamma\}} \langle \phi_0^{(0)} | \hat{H}_1 | \phi_0^{(0)} \rangle$$

k-space sums, FS integrations

$$+ \sum_\Gamma E_\Gamma\{A,B,C\} m_\Gamma$$

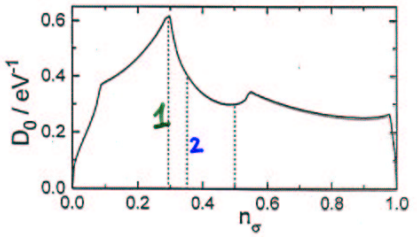
Racah Par.

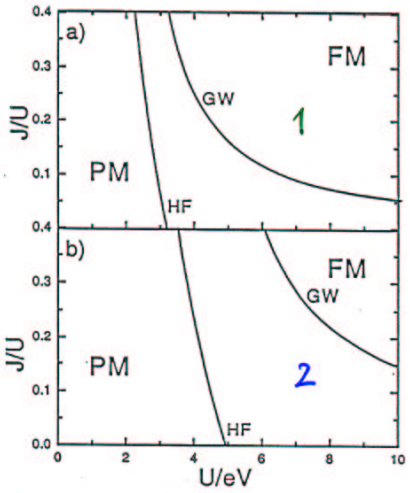
Variation of m_Γ ("internal" VP) $\approx$ 200 - 1000 for d-shell

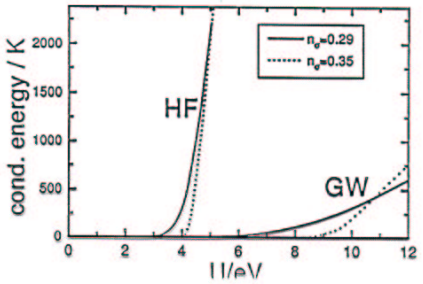
$\Rightarrow m_\Gamma^{(0)}$, $q_\sigma^{(0)}$

$$\hat{H}_{\mathrm{eff}}^{(1)} = \sum_{ij} \sqrt{q_{i\sigma}^{(0)}} \sqrt{q_{j\sigma'}^{(0)}}\, t_{ij}^{\sigma\sigma'} \hat{c}_{i\sigma}^{+} \hat{c}_{j\sigma'} + \sum_{i\sigma} (\varepsilon_{i\sigma} + \Delta_{i\sigma}) \hat{n}_{i\sigma}$$

$\Rightarrow |\phi_0^{(1)}\rangle$ and so on







two-band model for ferromagnetism

BWG, PRB 57, 6896 (1998)

Calculations for Iron Group Metals

- 9 - orbital basis: s, p, d
- tight binding model based on DFT results for paramagnetic cases
- correlation in the 3d - shell:

  atomic Racah Parameters A, B, C (fitted to atomic values)

  (spherical approx.)

$\Rightarrow$ 2^{10} multiplet states

($\approx$ 200 - 400 VP)

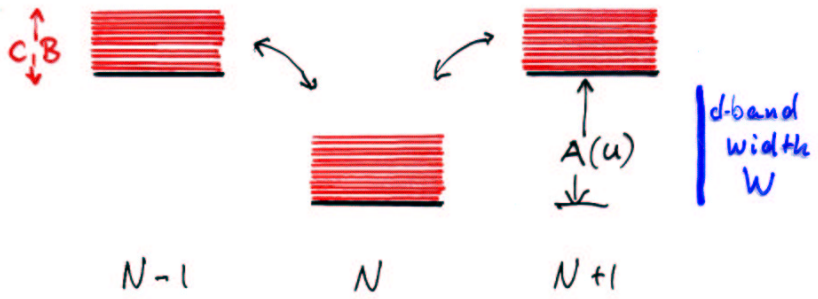
↑ pm ↑ fm afm

$\Rightarrow$ further VP in HF trial wave function

exchange fields, orbital dependent

$e_g - t_{2g}$

chemical potentials to fix n_d, n_s, n_p



$A \approx 10\,eV$

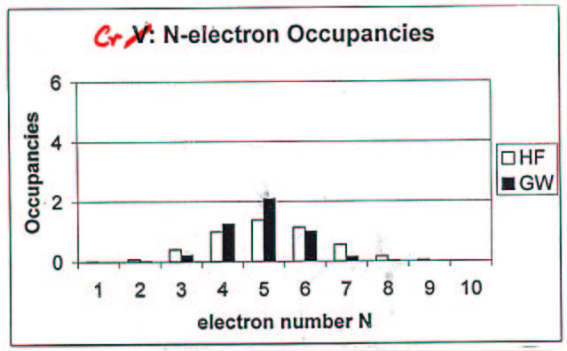
d-band width $\approx 6\,eV$

width of multiplets $\approx 2\text{-}3\,eV$

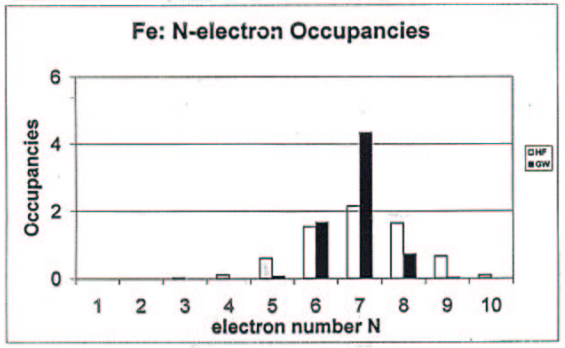
s,p-d hybridisation $\approx 1.5\,eV$

energy gain compared to HF $\approx 2\text{-}5\,eV/atom$

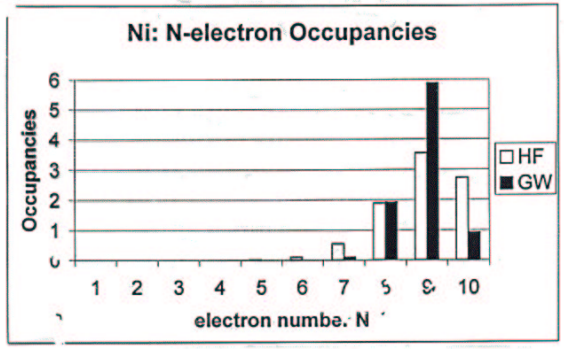
E_{Cond} $\approx 10 - 100\,meV$



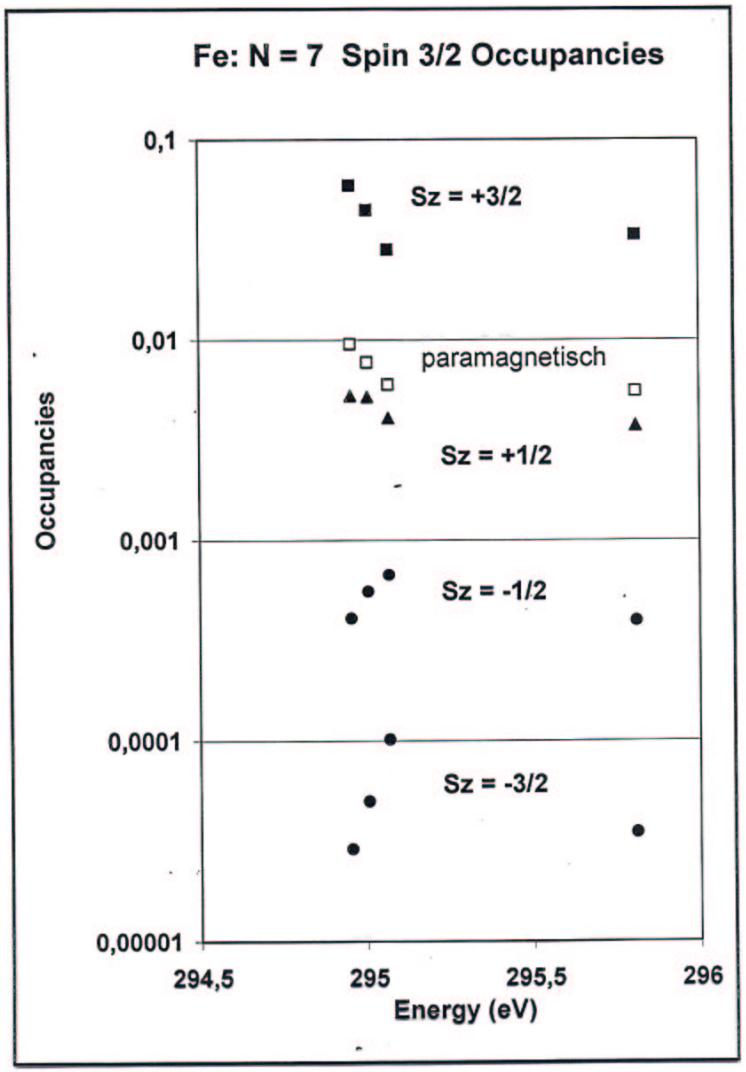
A = 5 eV



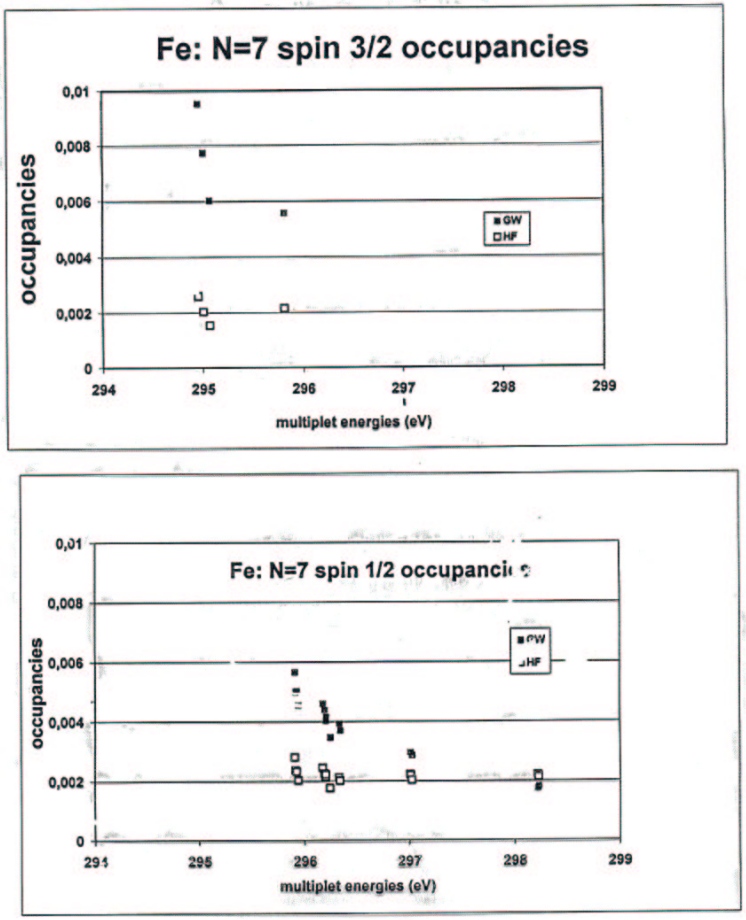
A = 10



A = 14



paramagnetic



Problems with Nickel

	Exp.	SDFT
d-band Width	3.3 eV	4.5 eV
$N^*(E_F)$ (electronic specific heat)	3.0 eV^{-1}	1.9 eV^{-1}
exchange splitting	small anisotropic (150-300 meV)	Large isotropic (600 meV)
spin-only magnetic moment	0.55 μ_B	0.59 μ_B
Fermi surface (minority)	no X_2 hole	X_2 hole ellipsoid
t_{2g}/e_g fraction of magnetic moment	81/19	74/26
(p) L_2'	-1.0 eV	-0.35 eV
[(s) Γ_1	-8.8 eV	-8.9 eV]

Total energy studies for ferromagnetic nickel

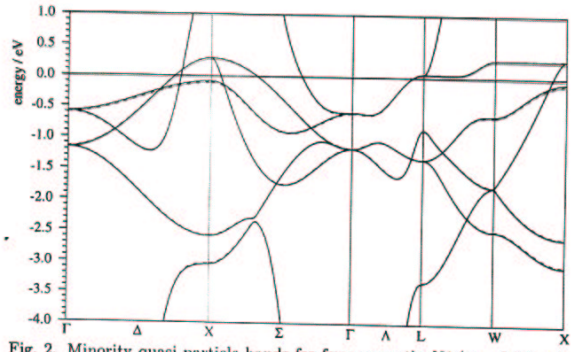


Fig. 2. Minority quasi particle bands for ferromagnetic Ni ($\mu = 0.55\ \mu_B$), obtained from the Gutzwiller DFT calculations using either $C = 0.4$ eV (full lines) or $C = 1.0$ eV (dashed lines). The two calculations differ only on a scale of a few meV.

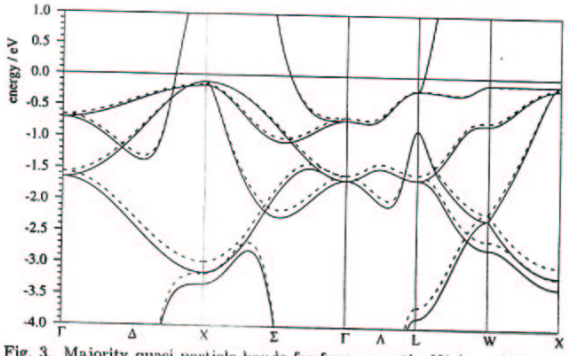


Fig. 3. Majority quasi particle bands for ferromagnetic Ni ($\mu = 0.55\ \mu_B$) from the $C = 0.4$ eV (full lines) and the $C = 1.0$ eV calculations (dashed lines). The two calculations differ on a scale of 10-100 meV.

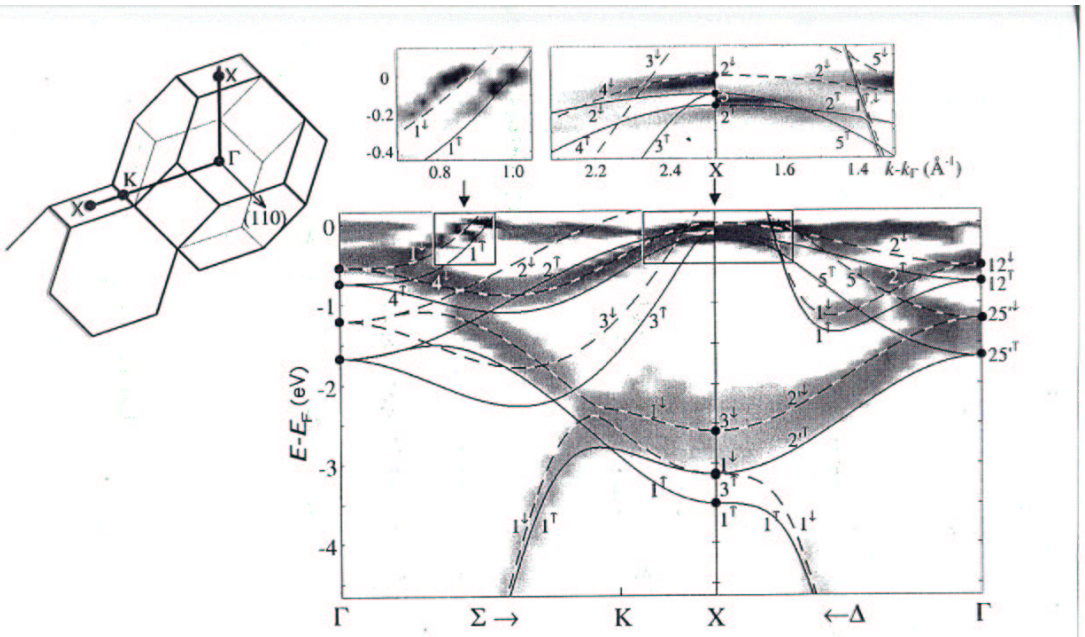


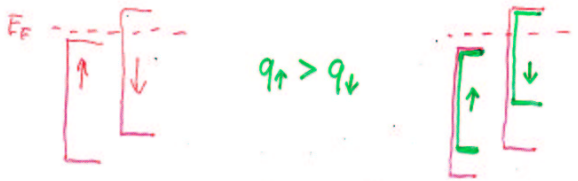
FIG. 1: Grey-scale plot of the negative second derivative of the ARPES intensity for nickel with respect to energy, $-d^2I/dE^2$, on a logarithmic scale (insets: linear scale) for the ΓKX and ΓX directions of the BZ. The dispersionless structure at E_F is due to a residual Fermi edge resulting from indirect transitions. Some bands (Δ_2, X_1, Σ_2, Σ_3, Σ_1 towards Γ) are not seen due to unfavorable matrix elements, depending on geometry and chosen final state. Theoretical curves are G-DFT III, see table I.

$n_d = 8.87$ $n_d = 8.78$ $\mu = 0.55\mu_B$

Symmetry	Character	Experiment	G-DFT II	G-DFT III	SDFT
$\langle\Gamma_1\rangle$	S	8.90±0.30	8.89	8.86	8.96[−0.11]
$\langle\Gamma_{25'}\rangle$	T	1.30±0.06	1.52[0.62]	1.44[0.46]	1.99[0.43]
$\langle\Gamma_{12}\rangle$	E	0.48±0.08	0.71[0.29]	0.65[0.195]	0.86[0.41]
$\langle X_1\rangle$	sE	3.30±0.20	3.39[0.50]	3.31[0.36]	4.37[0.20]
$\langle X_3\rangle$	T	2.63±0.10	2.95[0.72]	2.86[0.54]	3.82[0.37]
$X_{2\uparrow}$	E	0.21±0.03	0.27	0.165	0.35
$X_{2\downarrow}$	E	0.04±0.03	0.02	0.01	−0.09
$X_{5\uparrow}$	T	0.15±0.03	0.24	0.10	0.23
$\Delta_{e_g}(X_2)$	E	0.17±0.05	0.25	0.155	0.44
$\Delta_{t_{2g}}(X_5)$	T	0.33±0.04	0.49	0.38	0.56
$\langle K_2\rangle$	spTe	2.48±0.06	2.64[0.66]	2.59[0.50]	3.37[0.32]
$\langle K_4\rangle$	pE	0.47±0.03	0.58[0.28]	0.51[0.185]	0.70[0.41]
$\langle L_1\rangle$	sT	3.66±0.10	3.59[0.68]	3.51[0.515]	4.56[0.23]
$\langle L_3\rangle$	tE	1.43±0.07	1.58[0.47]	1.51[0.34]	2.02[0.40]
$L_{3\uparrow}$	Te	0.18±0.03	0.34[0.41]	0.215[0.30]	0.38[0.50]
$\langle L_{2'}\rangle$	P	1.00±0.20	0.29[0.0]	0.97[0.0]	0.24[−0.12]
$\langle W_1\rangle$	sE	0.65±0.10	0.76[0.30]	0.69[0.20]	0.94[0.39]
$W_{1'\uparrow}$	T	0.15±0.10	0.25[0.52]	0.11[0.38]	0.23[0.56]
$\langle\Lambda_{3;1/3}\rangle$	ptE	0.57[0.16±0.02]	0.73[0.32]	0.67[0.22]	0.90[0.42]
$\langle\Lambda_{3;1/2}\rangle$	ptE	0.50[0.21±0.02]	0.61[0.37]	0.55[0.26]	0.76[0.44]
$\langle\Lambda_{3;2/3}\rangle$	pTE	0.35[0.25±0.02]	0.39[0.41]	0.33[0.29]	0.49[0.48]

Δex(t2g) and Δex(eg) as function of band energy

SYM	wave fct	< E >	Δex
X5	t2g	0.11	0.36
Γ25'	t2g	-1.39	0.45
X3	t2g	-2.85	0.54
L1	s + t2g	-3.56	0.48
X2'	eg	-0.16	0.13
Γ12	eg	-0.68	0.17
K4	p + eg	-0.55	0.16
W2'	p + eg	-2.63	0.29
X1	s + eg	-3.22	0.34



offset by bigger orbital basis?

Summary of Ni Results

d-band width reduced by $\bar{q} \approx 0.7$ ($A = 9$ eV)

specific heat enhanced by $\approx 1/\bar{q}$

exchange splitting anisotropic:

$$\Delta_{ex}(t_{2g}) \approx 2 \cdot \Delta_{ex}(e_g)$$

result of variational procedure

why: t_{2g} NN hopping dominates

e-e interaction enforces strong fm (majority spin bands full)

system avoids highest anti-bonding states of minority spin bands which are t_{2g}.

⇒ large $\Delta_{ex}(t_{2g})$, small $\Delta_{ex}(e_g)$

GW → ? → SDFT Functional not flexible enough

GW → DFT Functional underestimates n_p (by ≈ 0.1e)

corrections lead to larger $n_d^{(hole)}$ smaller exchange splittings