From Clusters to Crystals: Application of Dynamical Mean-Field Theory to Materials

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in collaboration with:

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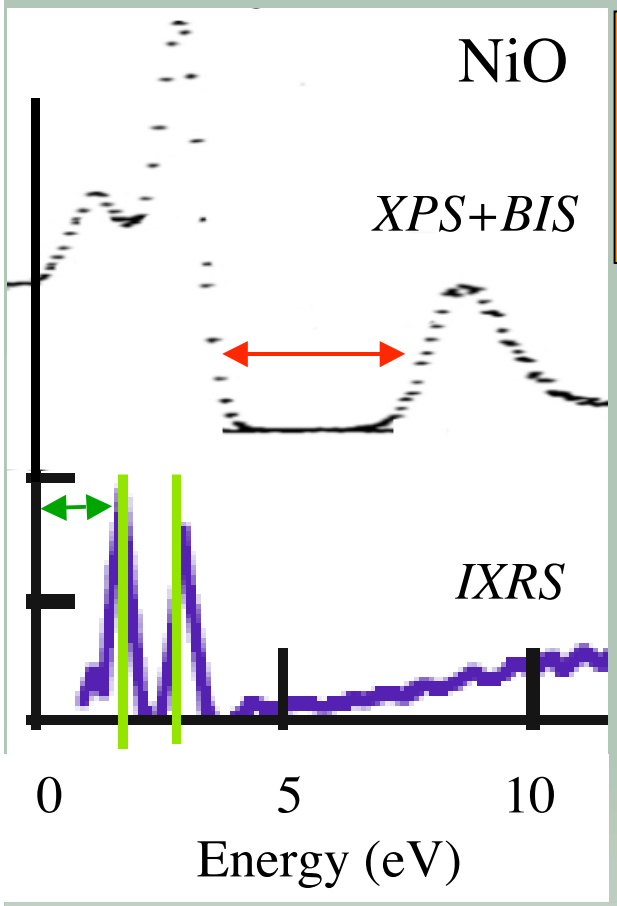
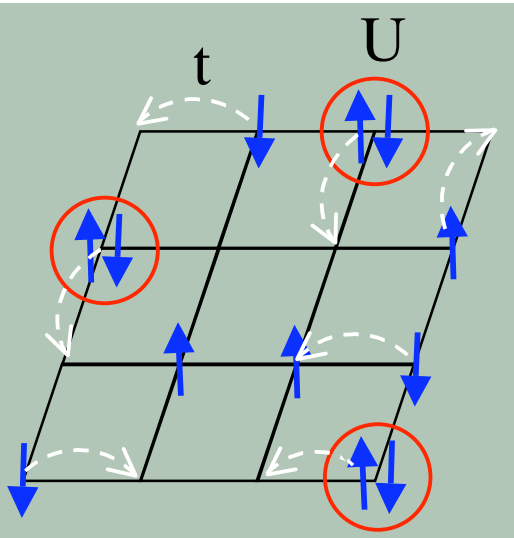
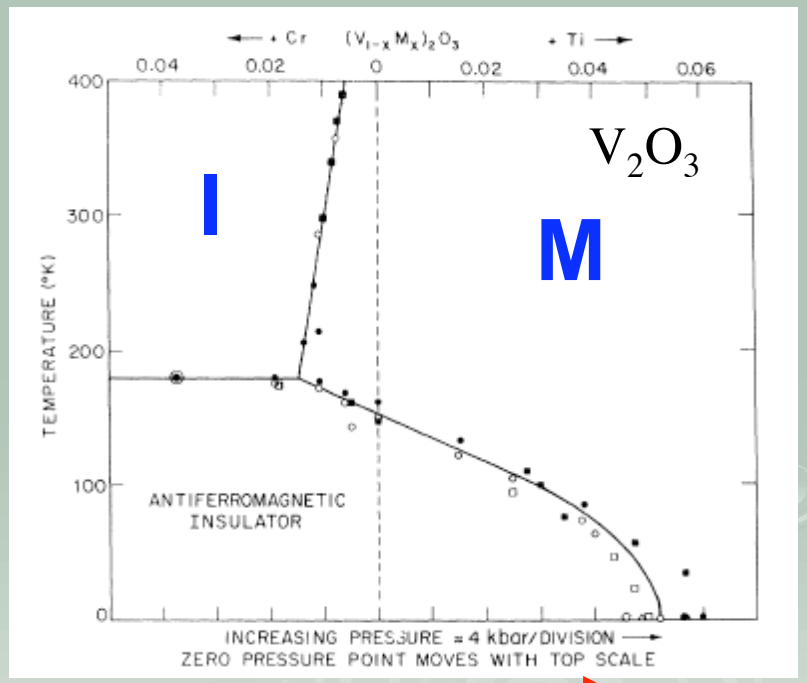
Hubbard model



$\Delta_{charge} \sim 4$ eV
$\Delta_{optic} \sim 1.5$ eV
$\Delta_{spin} \sim 0$





Pressure

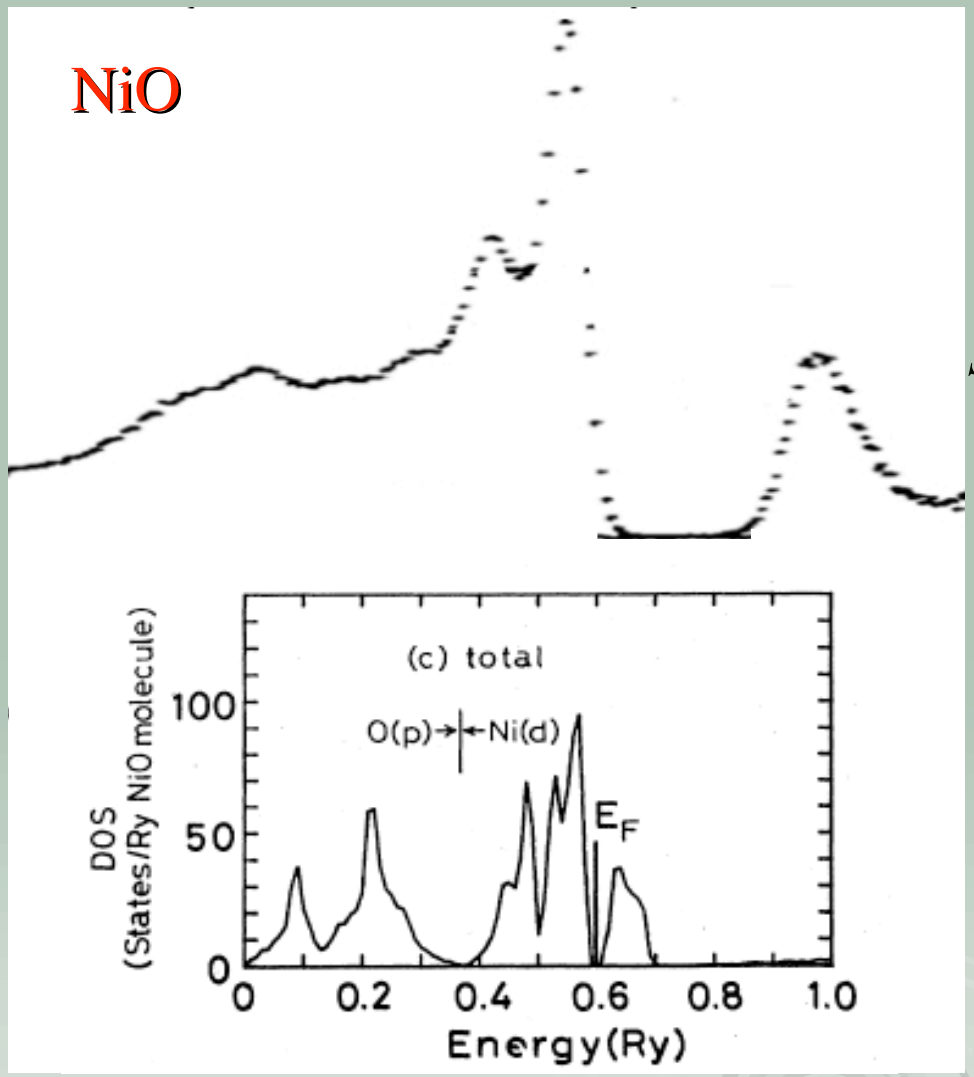
*Sawatzky & Allen, PRL **53**, 2339 (1984)*
*Hiraoka et al. EPJB **70**, 157 (2009)*

*McWhan et al. PRL **27**, 941 (1971)*

Outline

- Why do we need DMFT?
- Dynamical mean-field theory
- LDA+DMFT: applications to materials
- Correlated covalent insulator
- Summary

Mott insulators in band theory



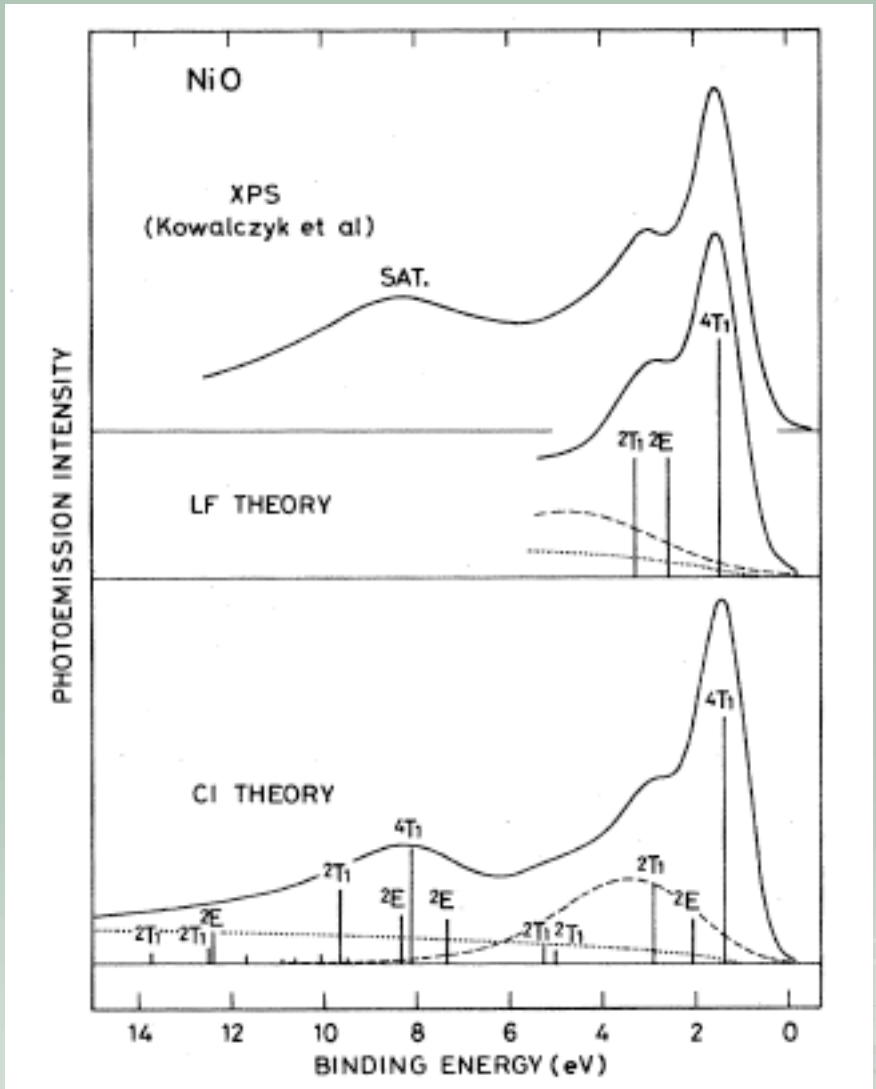
XPS+BIS experiment

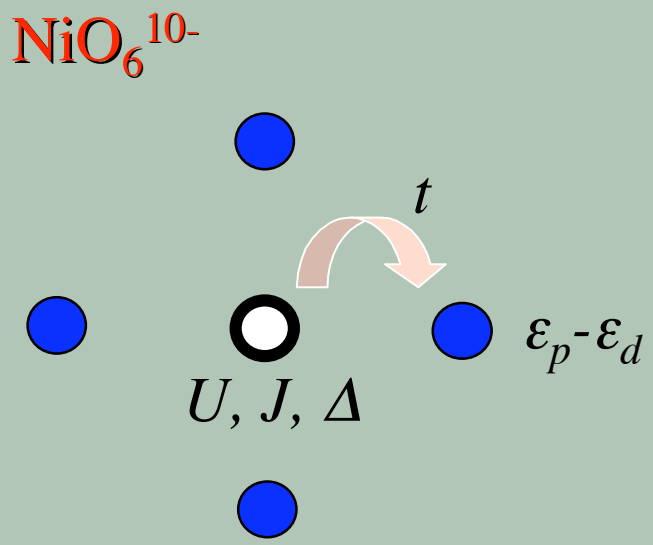
*Sawatzky & Allen, PRL **53**, 2339 (1984)*

LDA AFM calculation

*Terakura et al., PRB **30**, 4734 (1984)*

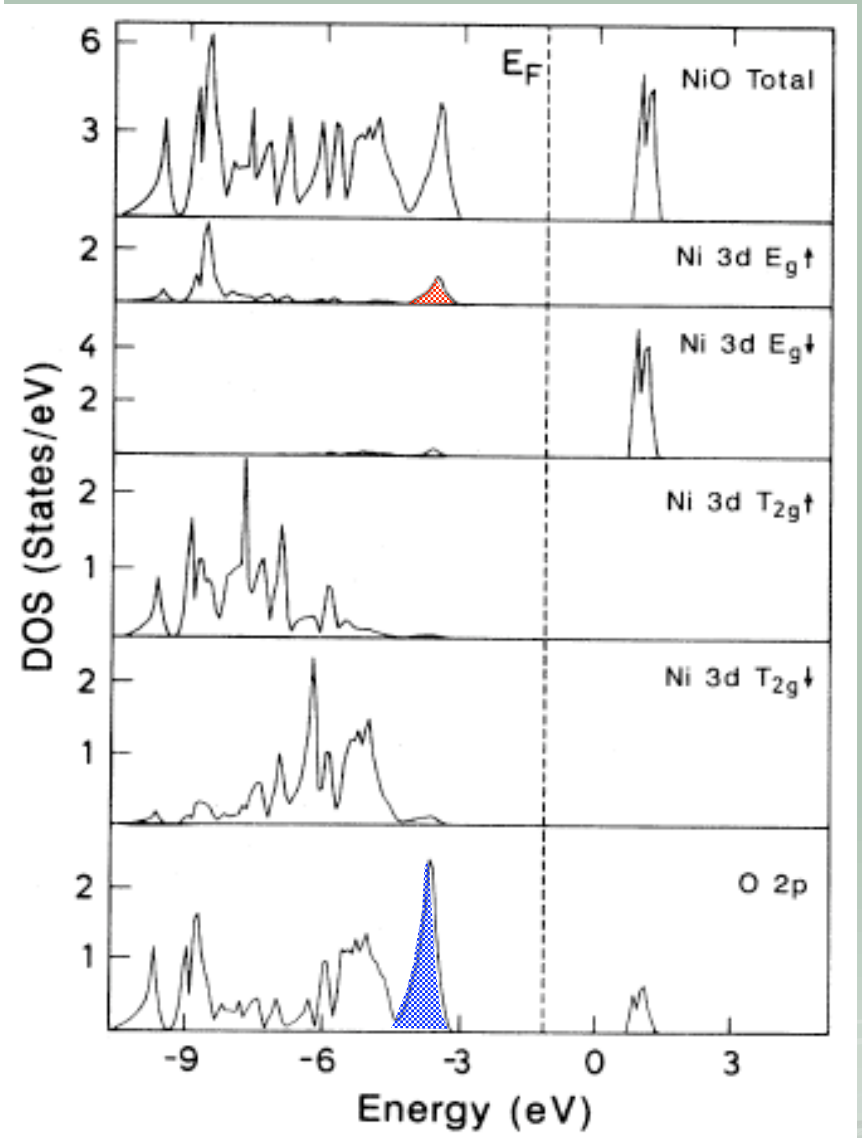
Cluster exact diagonalization





*Fujimori et al., PRB **29**, 5225 (1984)*

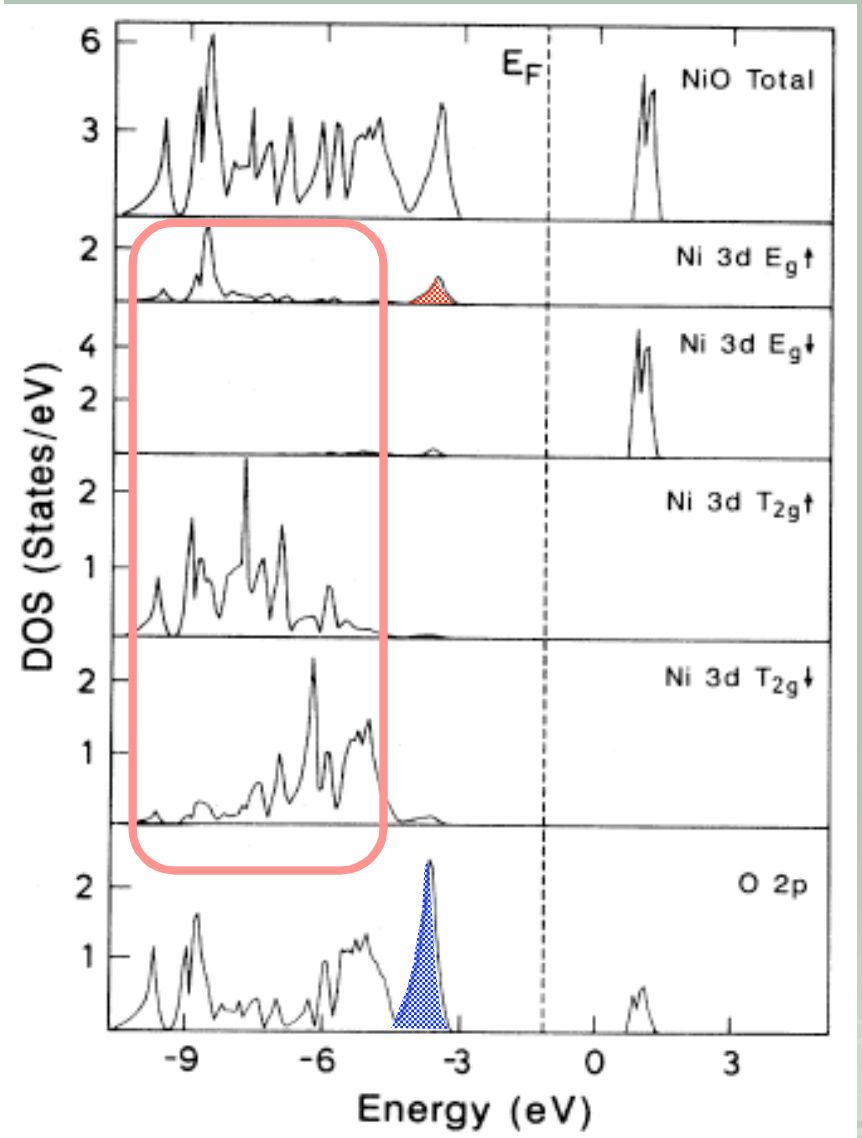
LDA+U



- Introduces orbitally dependent potentials
- Improves description of bulk properties or exchange integrals
- Applicable to states with broken symmetry
- Cannot describe paramagnetic Mott insulator, or doped Mott insulators

*Anisimov et al., PRB **44**, 943 (1991)*

LDA+U



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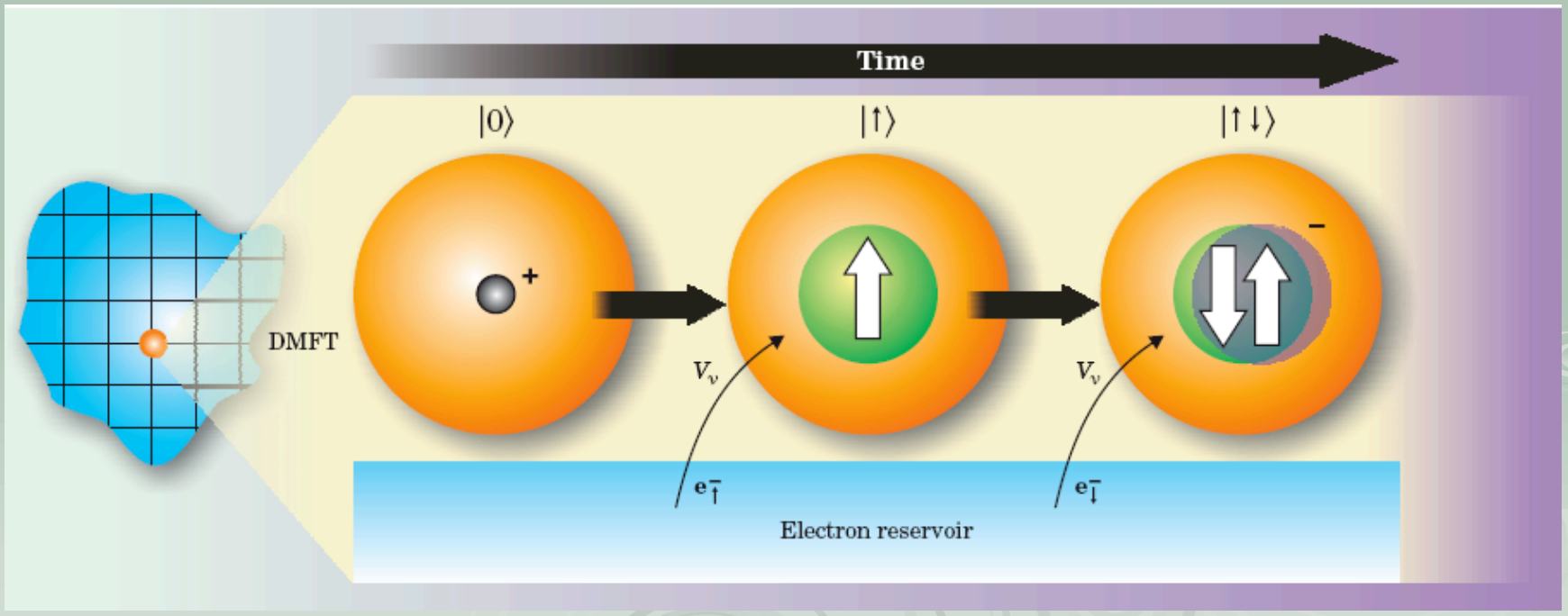
*Anisimov et al., PRB **44**, 943 (1991)*

Dynamical Mean-Field Theory (DMFT)

- Single out an atom from the lattice
- Replace the rest of the lattice by an effective medium
- Time resolved treatment of local electronic interactions
- Reconstruct lattice quantities



A. Georges et al. RMP ***68****, 13 (1996*) ***Physics Today*** (March 2004) Kotliar, Vollhardt

DMFT vs Weiss molecular field

$$\mathrm{H} = t_{ij} c_{i\sigma}^{+} c_{j\sigma} + U n_{i\uparrow} n_{i\downarrow}$$

$$G_{ii}(\tau) = -\left\langle c_i(\tau) c_i^{+}(0) \right\rangle$$

$$\mathrm{H}_{loc} = (\varepsilon_c - \mu) c_\sigma^{+} c_\sigma + U n_\uparrow n_\downarrow + V_\alpha \left(c_\sigma^{+} b_{\alpha\sigma} + H.c. \right) + \varepsilon_\alpha b_{\alpha\sigma}^{+} b_{\alpha\sigma}$$

$$\Rightarrow \Delta(\omega)$$

$$\Delta(\omega): \quad \left(\omega + \mu - \varepsilon_c - \Delta(\omega) - \Sigma(\omega)\right)^{-1} = \sum_{\mathbf{k}} \left(\omega + \mu - \varepsilon_{\mathbf{k}} - \Sigma(\omega)\right)^{-1}$$

$$\mathrm{H} = -J_{ij} S_i S_j - h S_i$$

$$m_i = \left\langle S_i \right\rangle$$

$$\mathrm{H}_{loc} = -h_{eff} S$$

$$h_{eff} = zJm + h$$

LDA $\Rightarrow$ Wannier projection: $\mathcal{H}_{\mathrm{LDA}}(\boldsymbol{k})$

$\Rightarrow$ constrained LDA: $\boldsymbol{U}_{ij}$

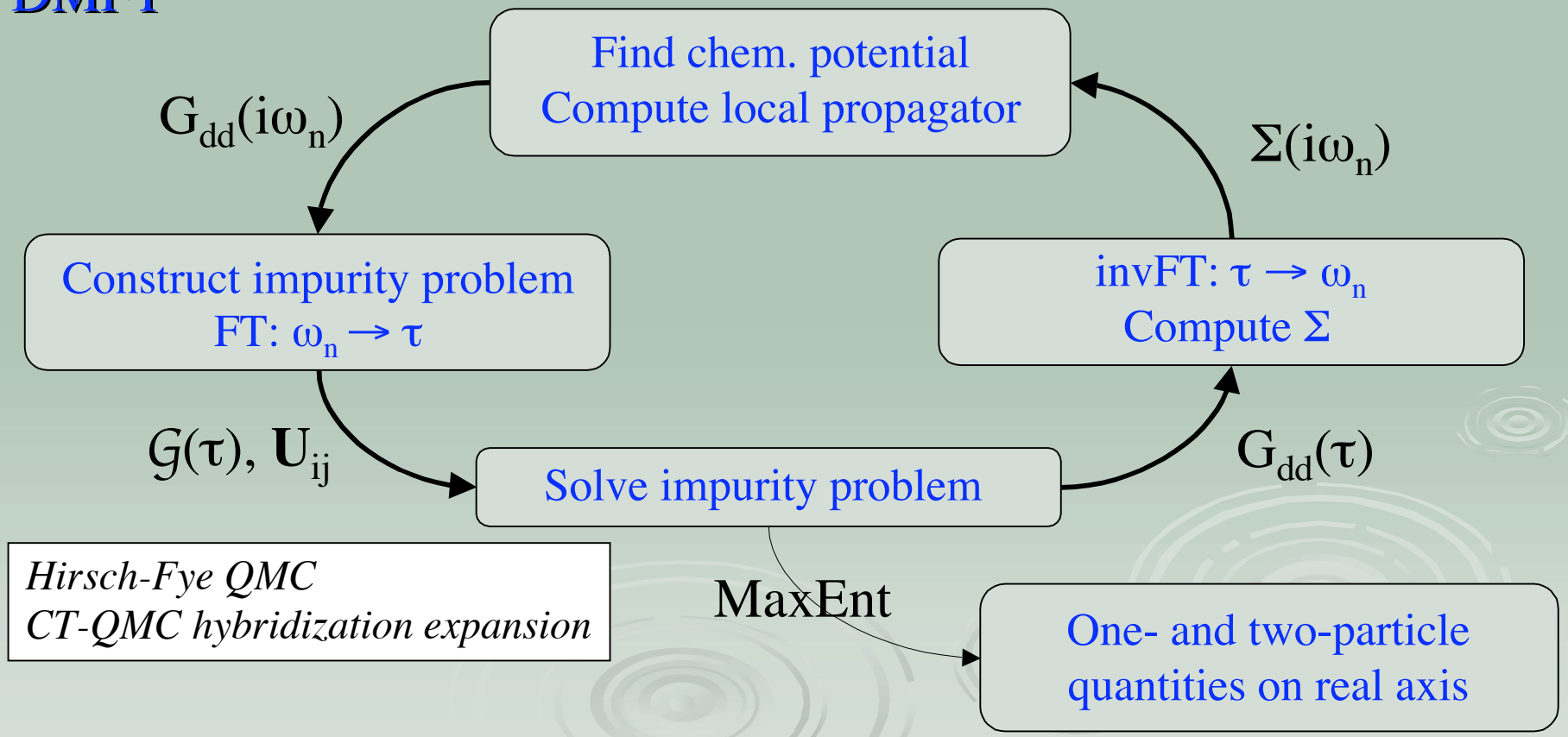
$\Rightarrow$ double counting : $\mathcal{H}_0(\boldsymbol{k}) = \mathcal{H}_{\mathrm{LDA}}(\boldsymbol{k}) - E_{dc} n_{\mathrm{d}}$

$\mathcal{H} = \Sigma_{\boldsymbol{k}} \mathcal{H}_0(\boldsymbol{k}) + \Sigma_{\boldsymbol{R}} \boldsymbol{U}_{ij} n_{\boldsymbol{R}i} n_{\boldsymbol{R}\mathrm{j}}$

FP-LMTO, PW paramagnetic solution

8x8 (MnO), 38x38 ($Fe_2 0_3$) matrices on 3375 k-points

DMFT

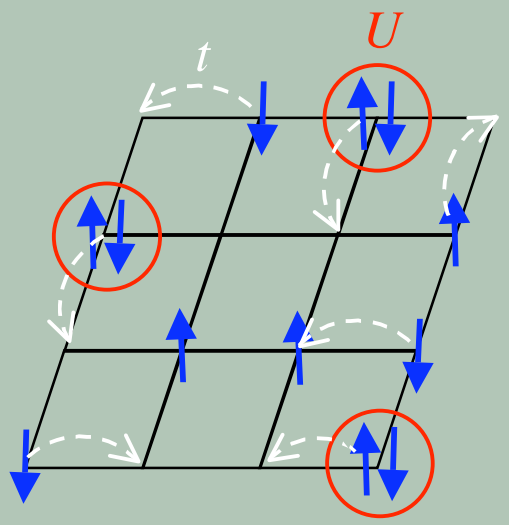


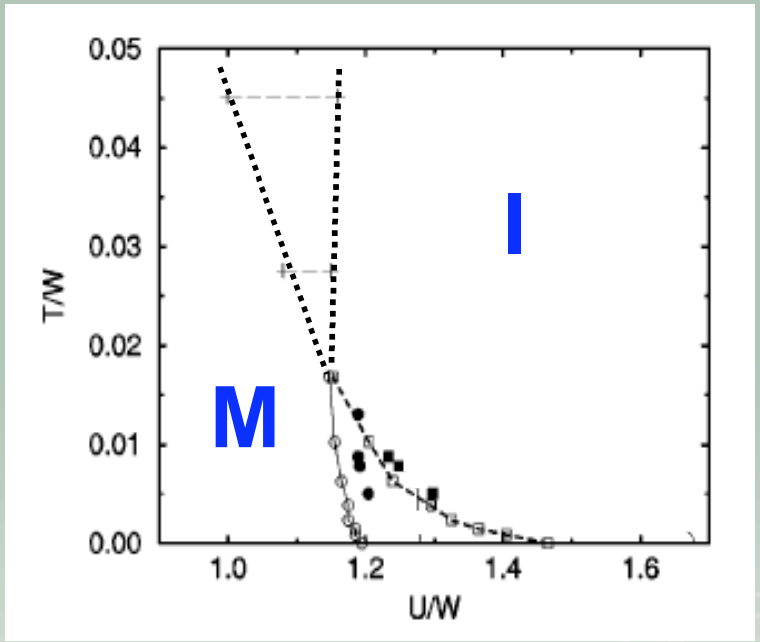
Hirsch-Fye QMC
CT-QMC hybridization expansion

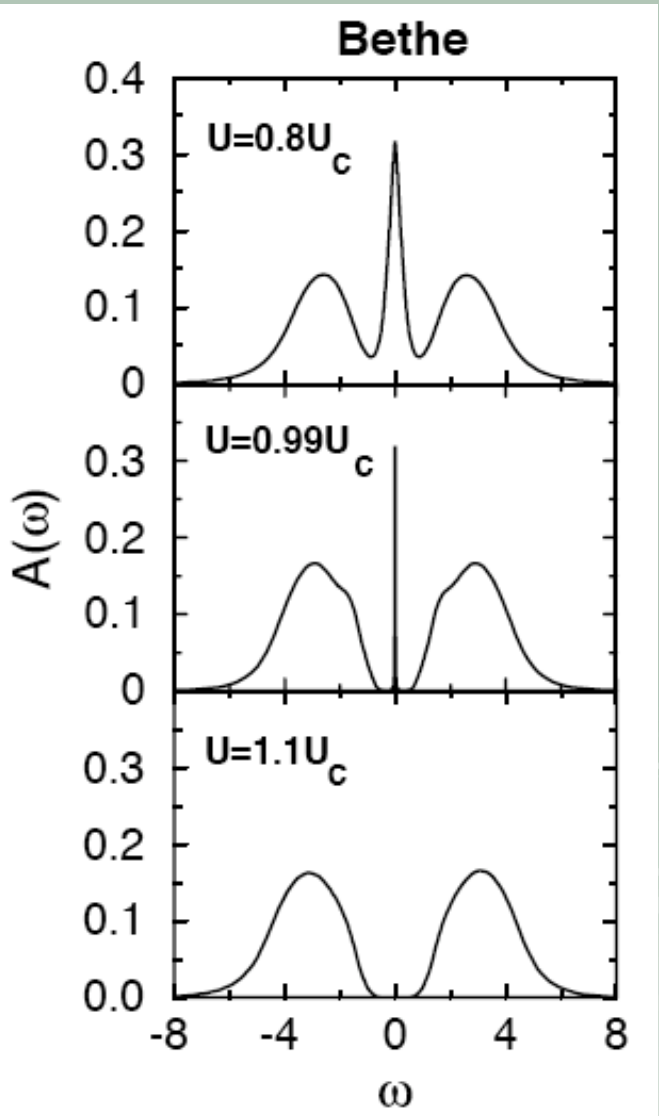
DMFT features

- many-body dynamics is local (no ***k***-dependence): $\Sigma(\omega)$, $\Gamma(\nu,\nu',\omega)$
- only single-particle self-energy $\Sigma(\omega)$ need for self-consistency
- DMFT is non-perturbative approach (exact in $D=\infty$)
- DMFT contains T-dependence beyond Fermi-Dirac due to local Kondo physics
- DMFT captures local correlations $\langle A_i B_i \rangle \neq \langle A_i \rangle \langle B_i \rangle$

DMFT for single band Hubbard model





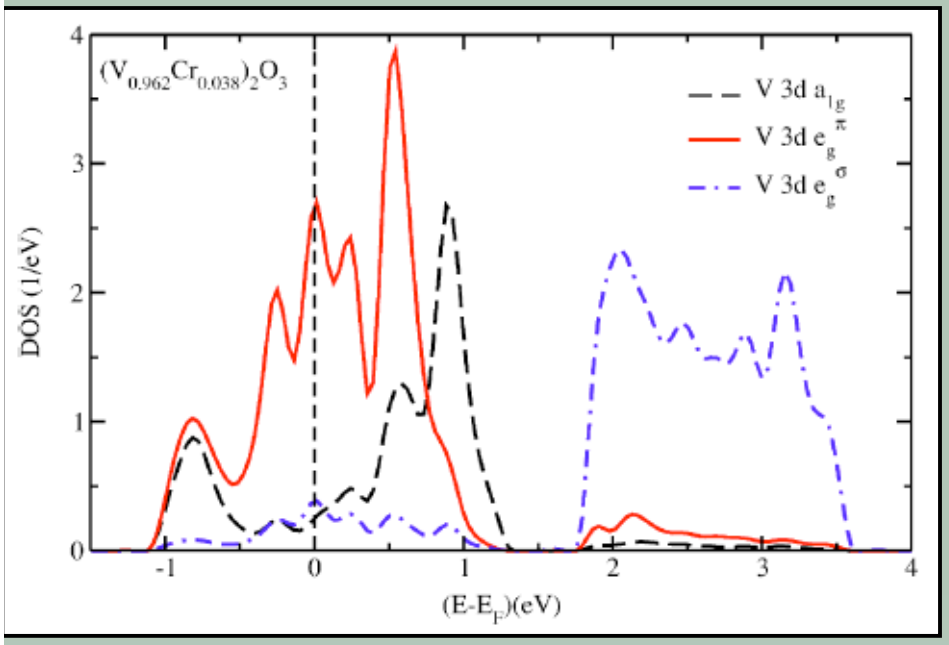


*Bulla et al. PRB **64**, 045103 (2001)*

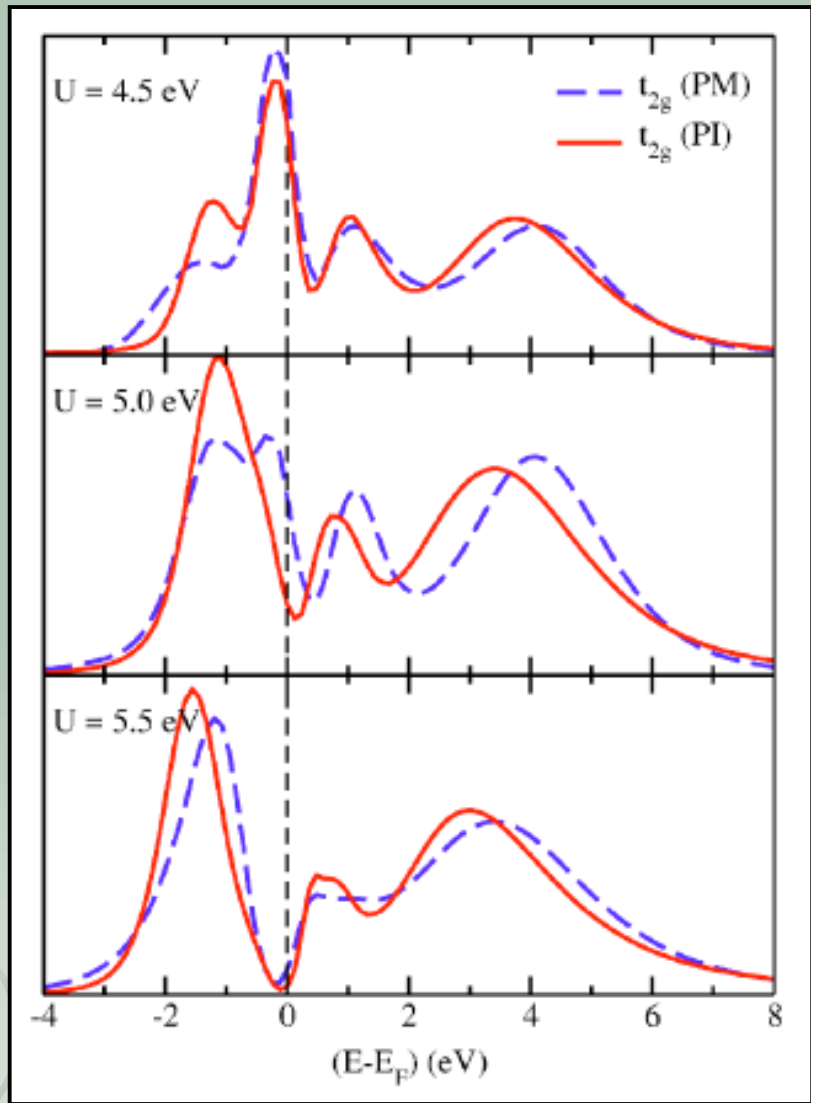
*for review A. Georges et al. RMP **68**, 13 (1996)*

Mott transition - V_2O_3

LDA

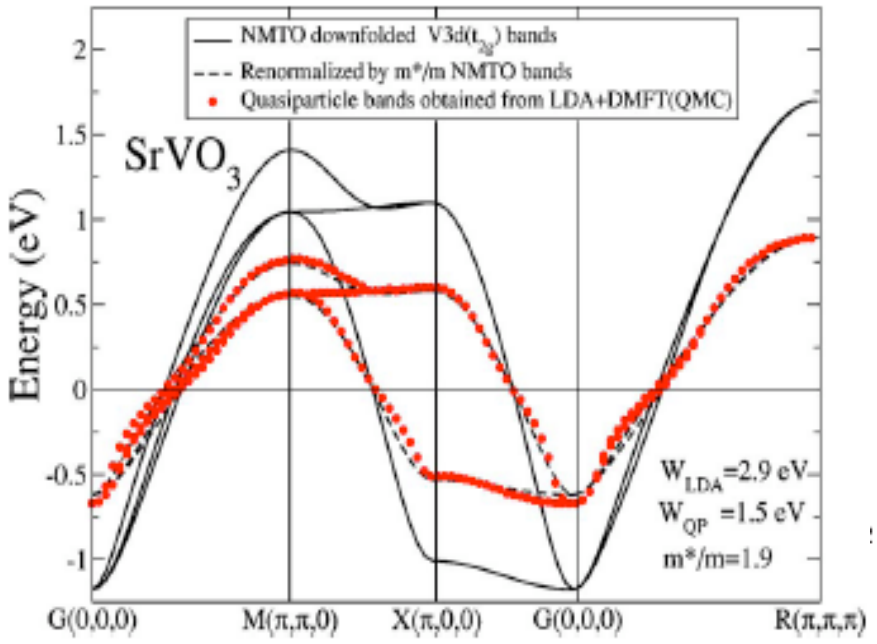


LDA+DMFT



*Keller et al. PRB **70**, 205116 (2004)*)

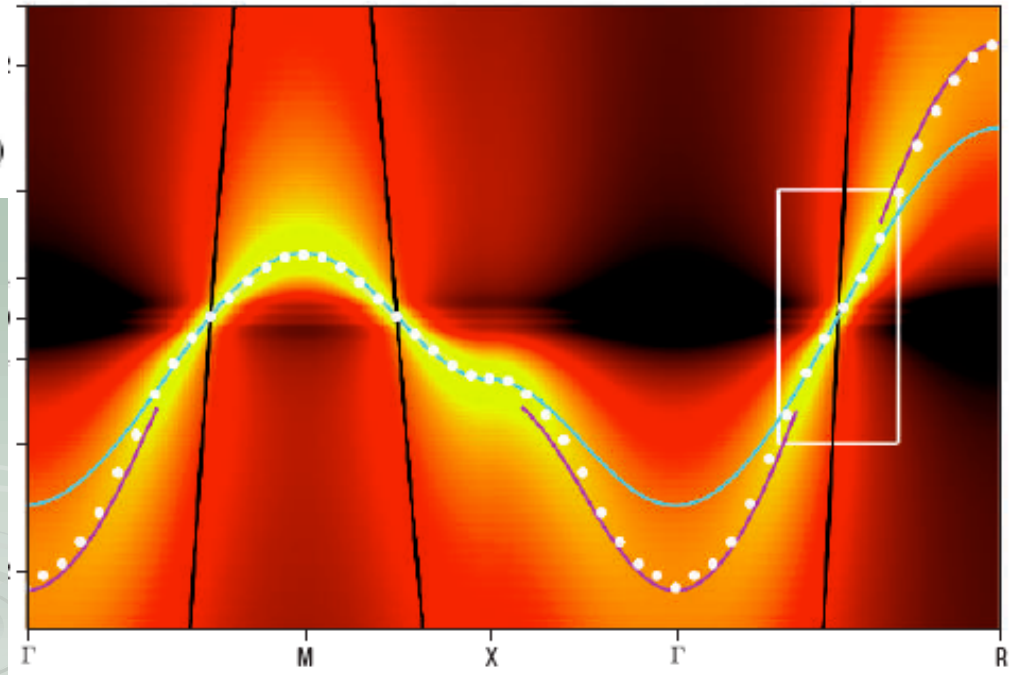
Quasiparticle renormalization



Nekrasov et al. PRB ***73****, 155112 (2006)*

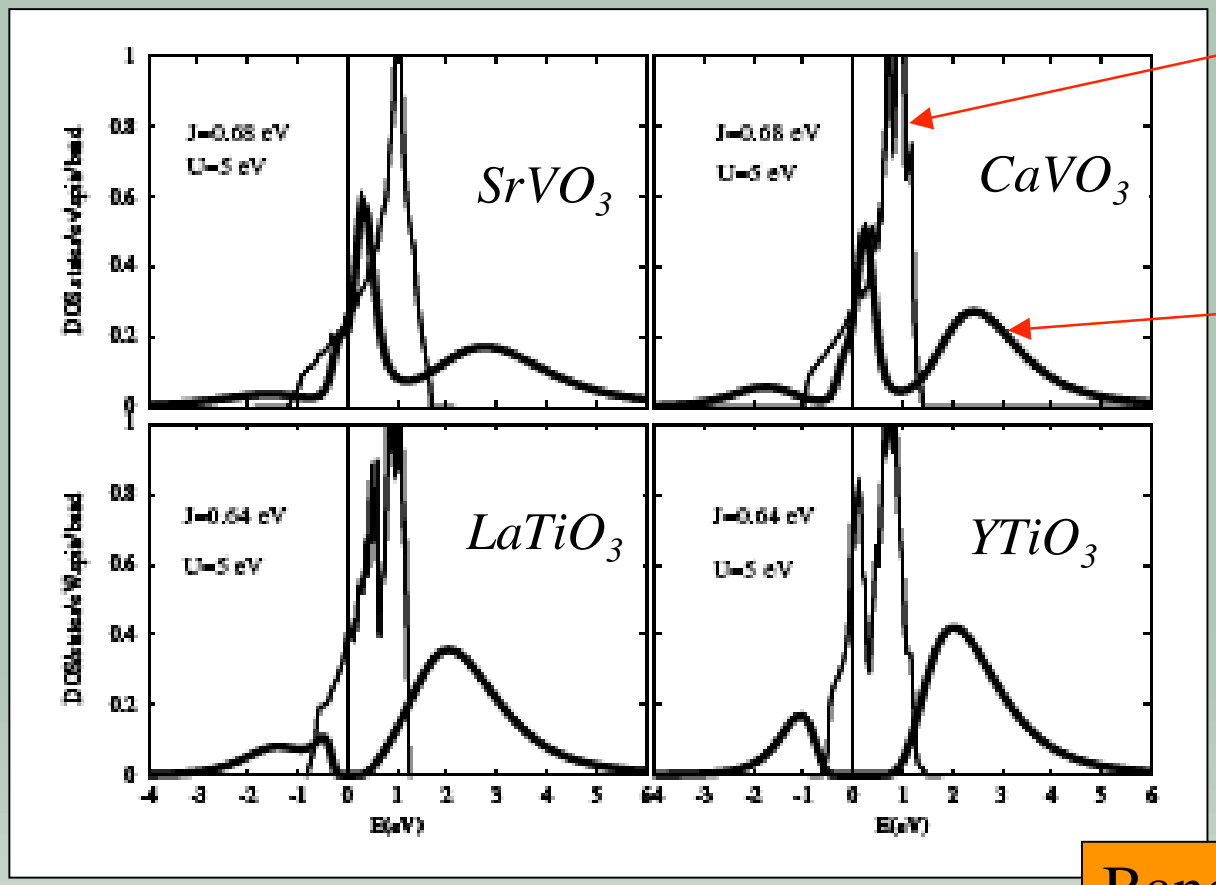
Materials motivate model studies

Byczuk et al. Nat. Phys. ***3****, 168 (2007)*



Crystal-field effects

Orbital fluctuations in d^1 perovskites



LDA

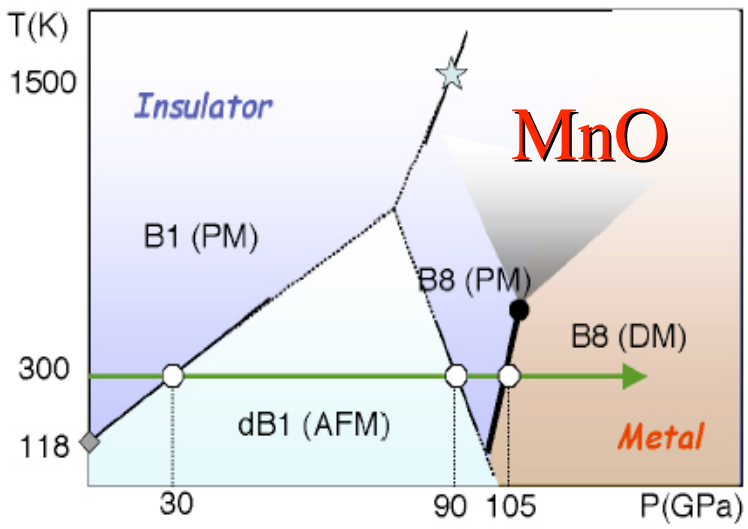
LDA+DMFT

Bandwidth is renormalized while crystal field is not

Pavarini et al., Phys. Rev. Lett. ***92****, 176403 (2004)*

Moment collapse and Mott transition under pressure

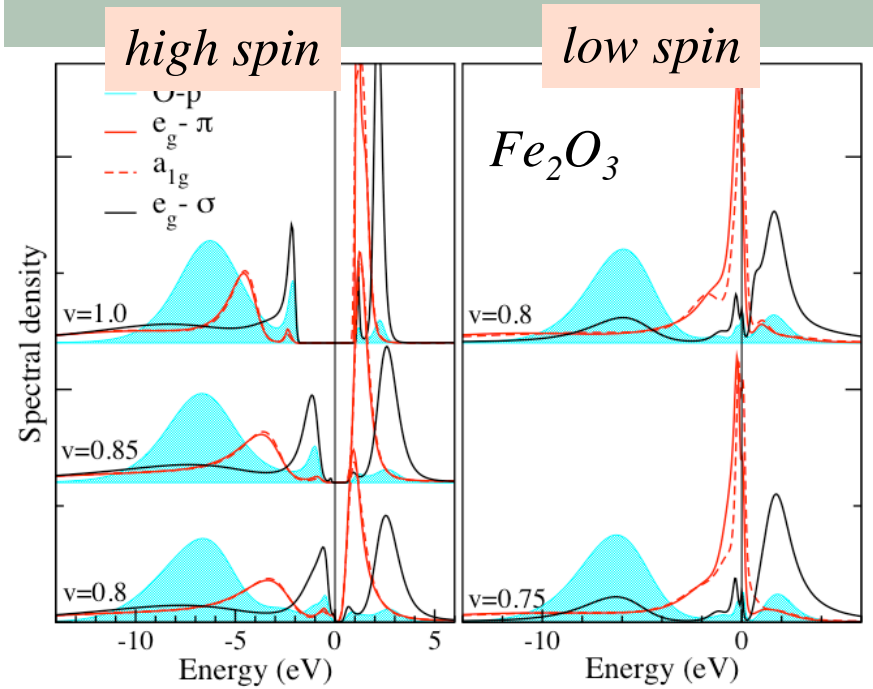
(crystal-field + on-site exchange J)



*Yoo et al., PRL. **94**, 115502 (2005)*

- moment collapse
- insulator -> metal transition
- volume collapse
- structural transition

FeO, CoO, Fe_2O_3, $BiFeO_3$, …



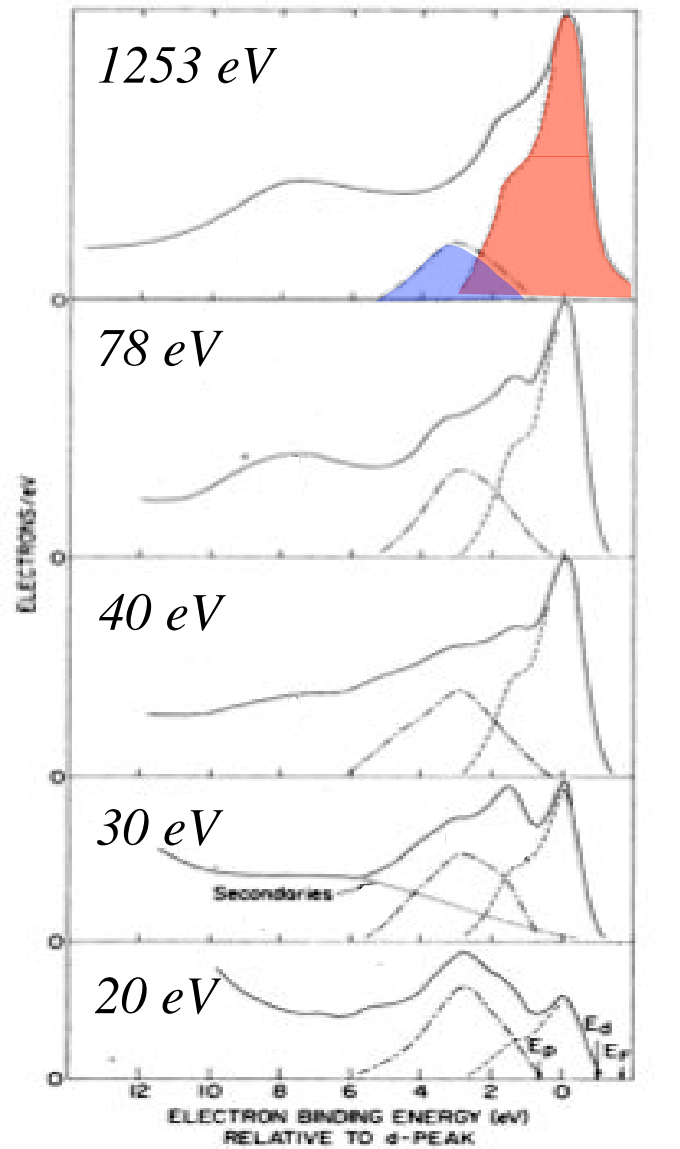
*JK et al. Nat. Mat. **7**, 198 (2008) … MnO*

*JK et al. PRL **102**, 146402 (2009) … Fe_2O_3*

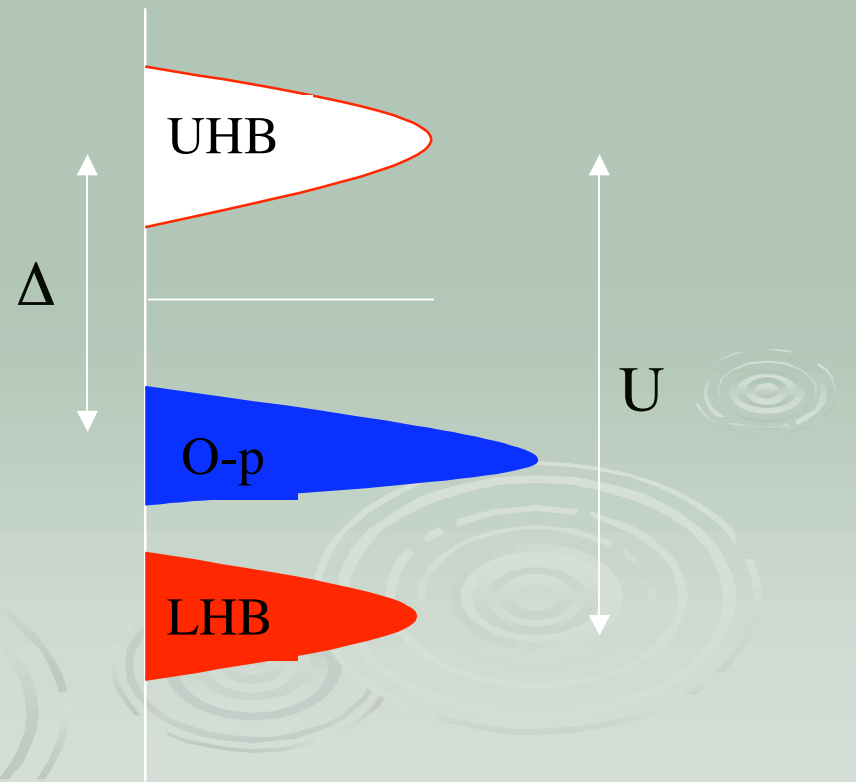
*Werner & Millis PRL **99**, 126405 (2007)*

*Lyubutin et al. PRB **79**, 085125 (2008) … $BiFeO_3$*

Charge-transfer materials: NiO

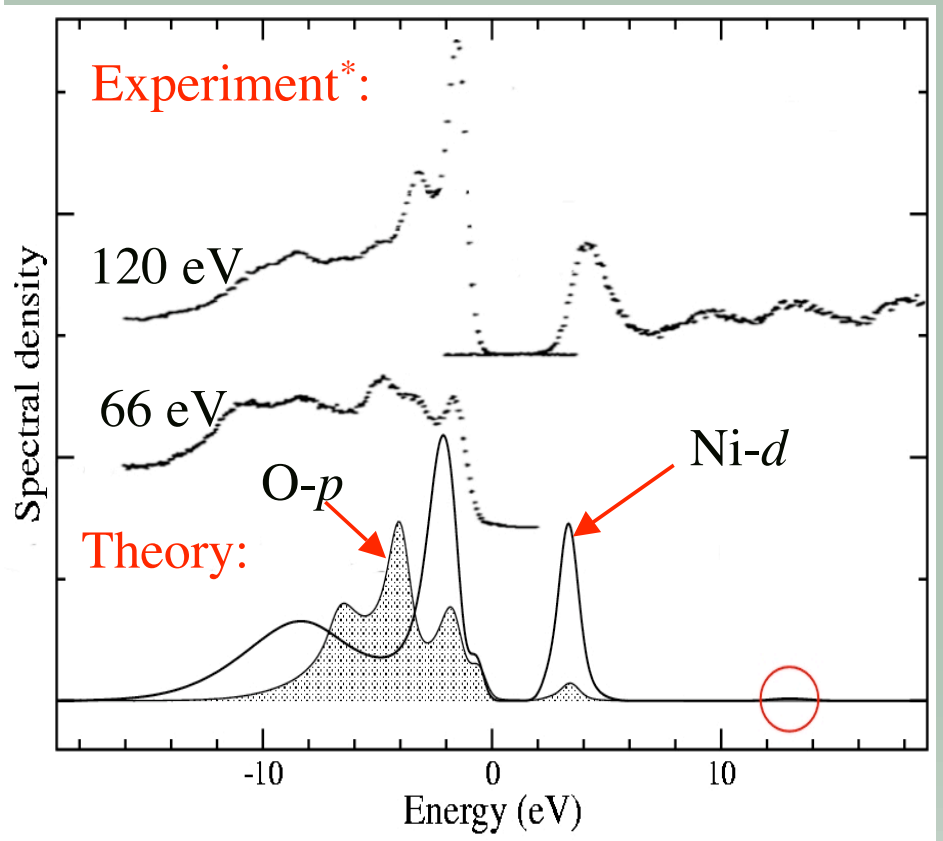


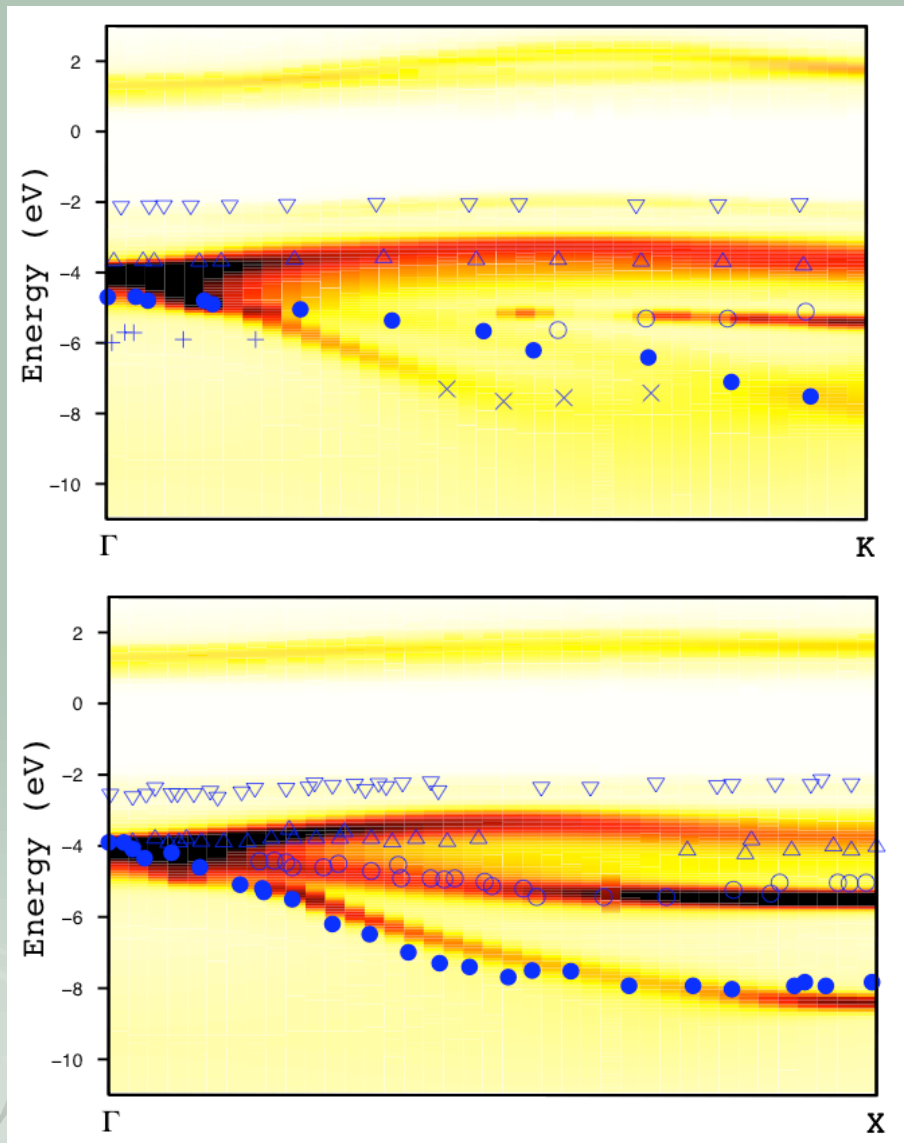
- Is NiO charge-transfer insulator?
- How does hole doping affects the spectrum?
- Role of AFM order?



Eastman & Freeouf, PRL ***34****, 395 (1974)*

Charge-transfer insulators: NiO
(*p-d* hybridization)

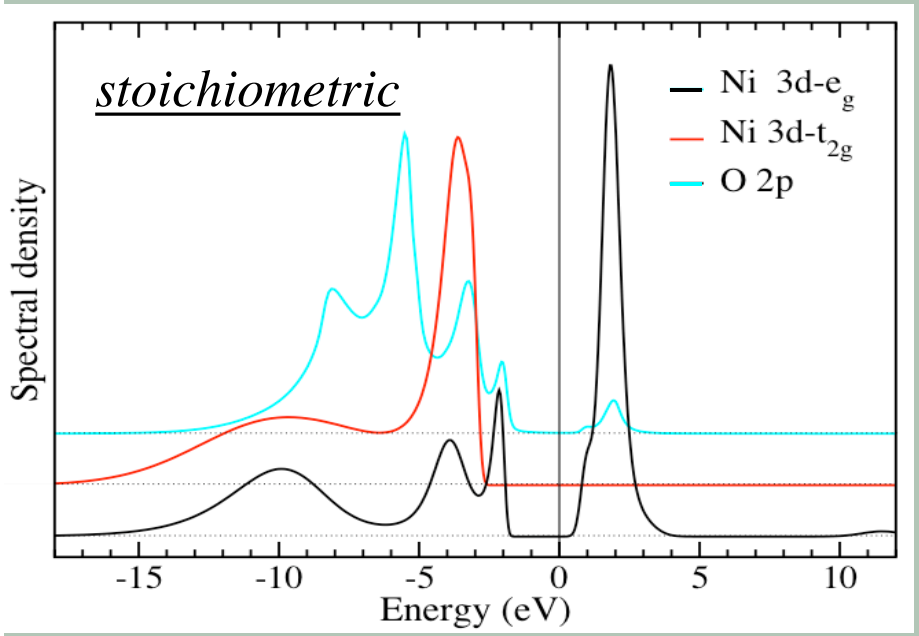




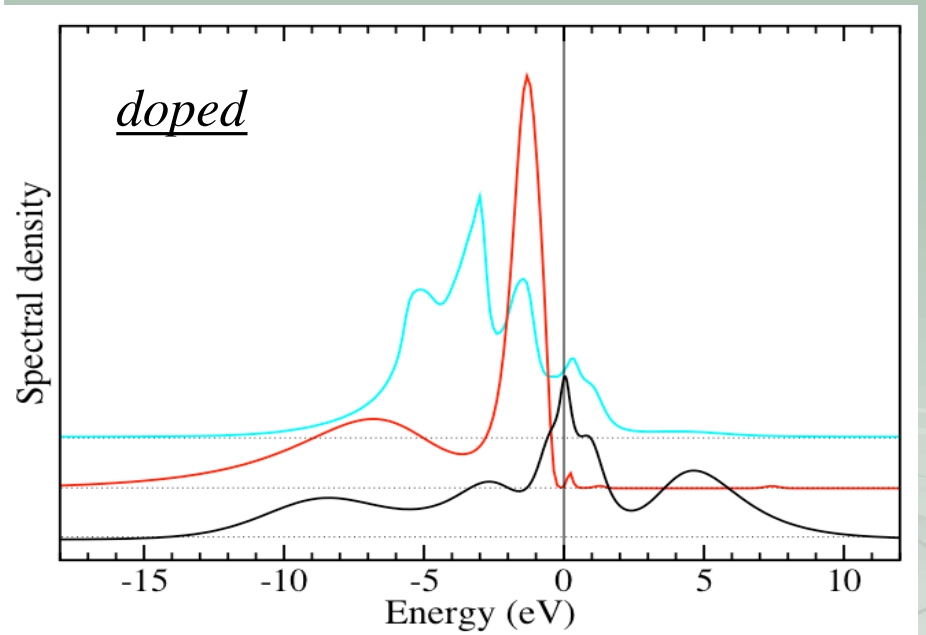
JK et al. PRB ***75****, 165115 (2007),*
PRL

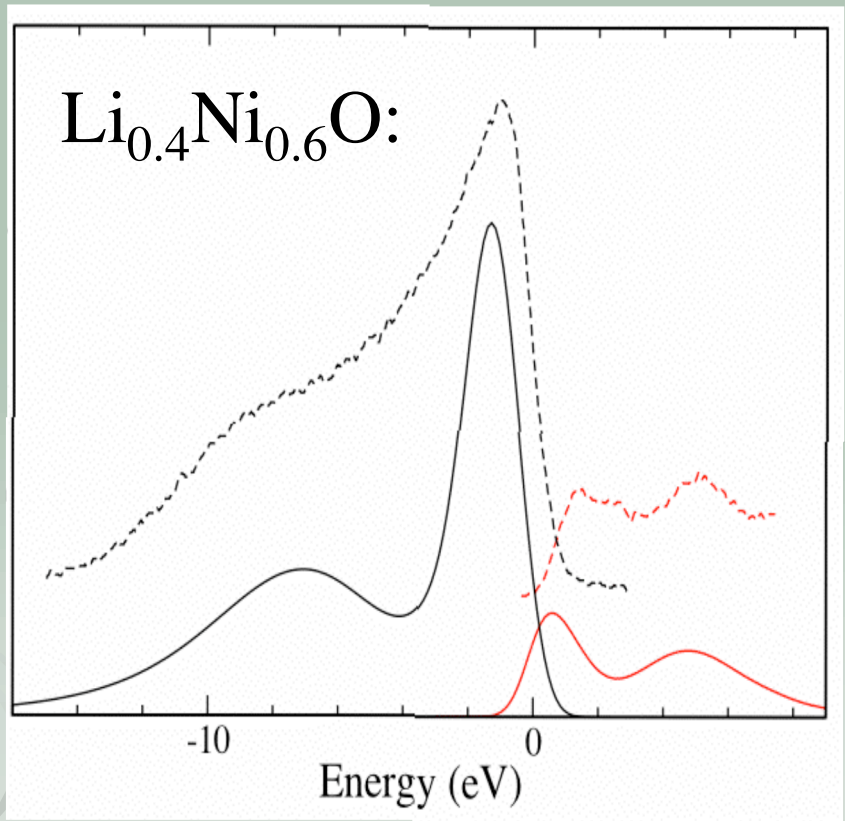
Exp. from Shen et al. PRB ***44****, 3604 (1991)*
and Sawatzky & Allen, PRL ***53****, 2339 (1984)*

Hole doping of NiO



n_h	e_g	t_{2g}	p
0.0	0.55	1.00	0.97
0.6	0.53	0.99	0.89
1.2	0.53	0.98	0.80

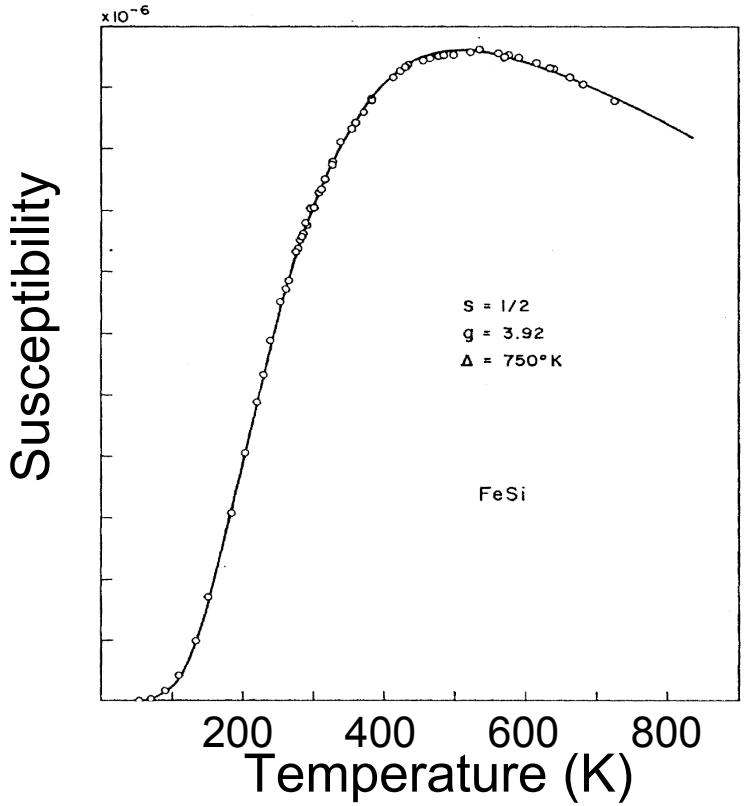




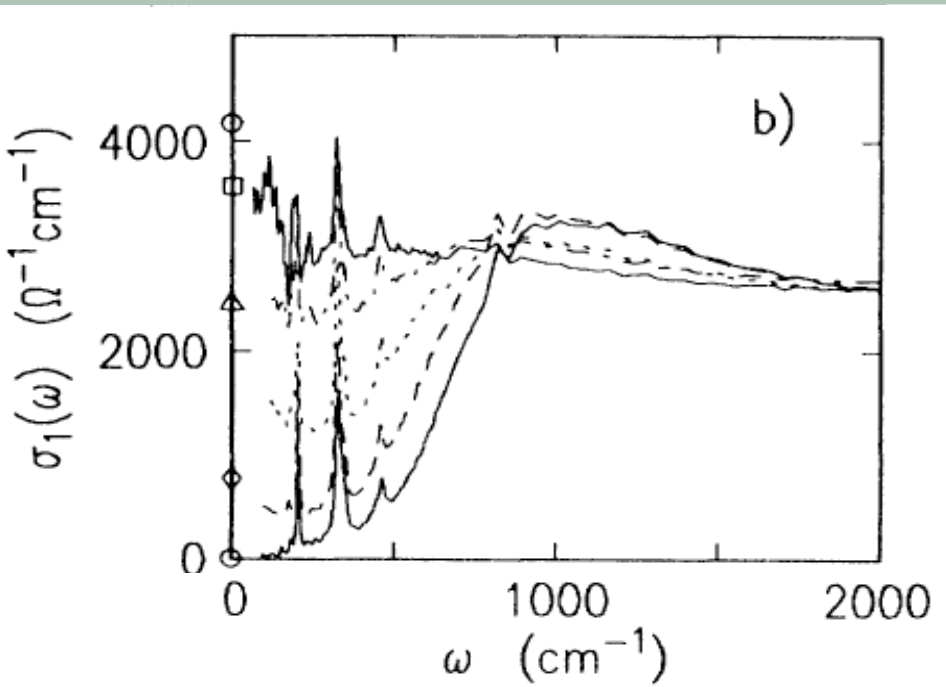
Correlated covalent insulator

- Minimal model description of FeSi.
- band insulator at low T, local moment bad metal at high T
- overestimation of gap by LDA (rare)
- Transition between band insulator and Mott insulator
- evolution of quasi-particle, charge- and spin- gaps as a function of U

Jaccarino et al. Phys. Rev. 1967



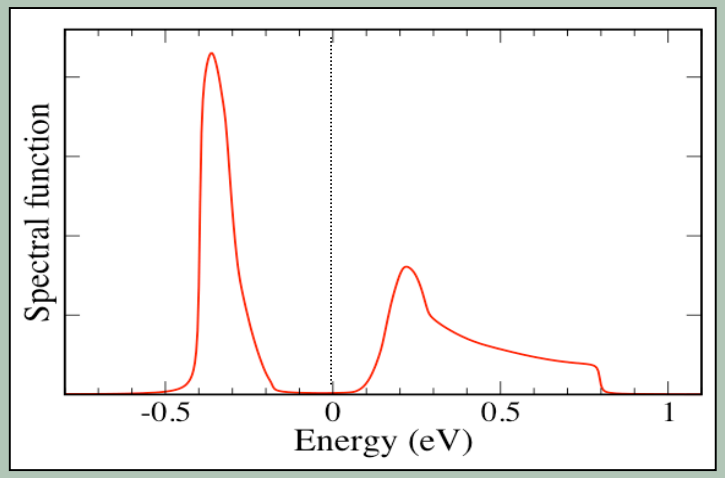
Schlesinger et al. PRL 1993



Correlated covalent insulator

Local spectral density:

MODEL:



+U=1.5 eV

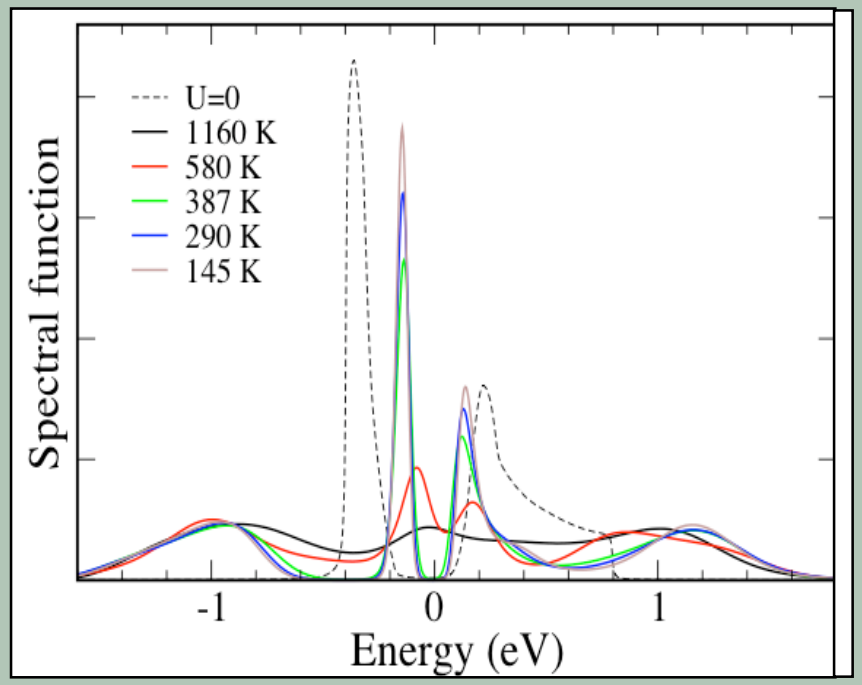
- 1 orbital (2 spins) per site, half-filling
- gap in non-interacting spectral function

  (origin of the hybridization gap is irrelevant for

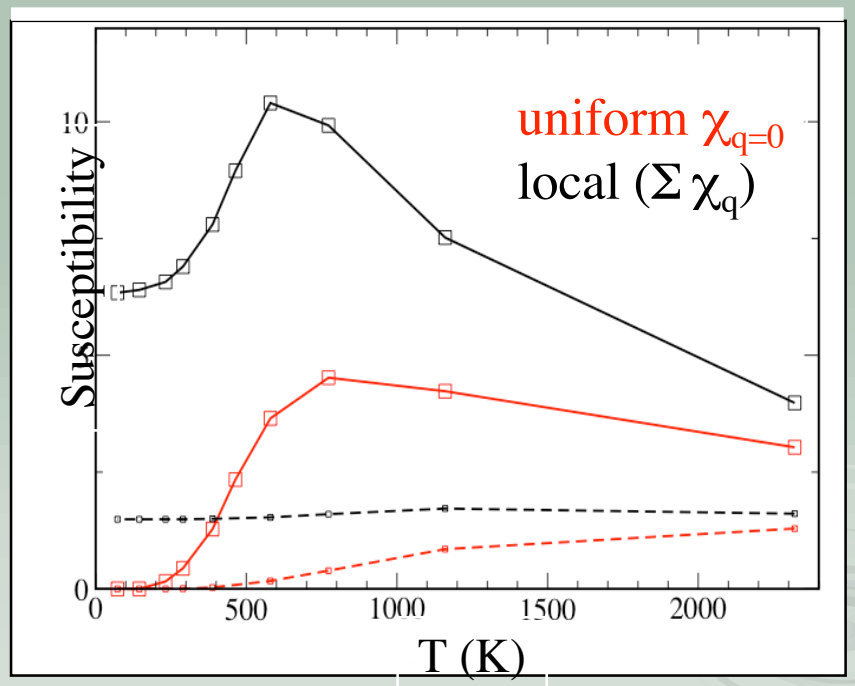
  local quantities and uniform susceptibility within DMFT)

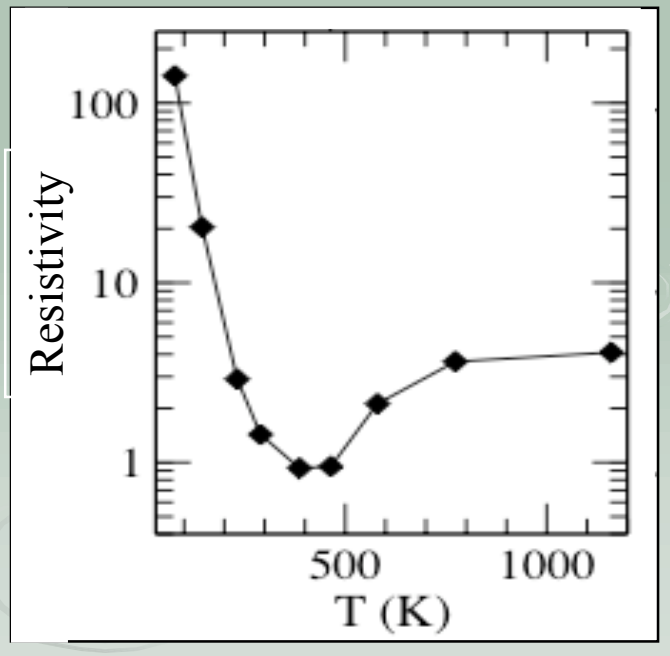
*JK & VI Anisimov PRB **78**, 033109 (2008)*

T-dependent quantities

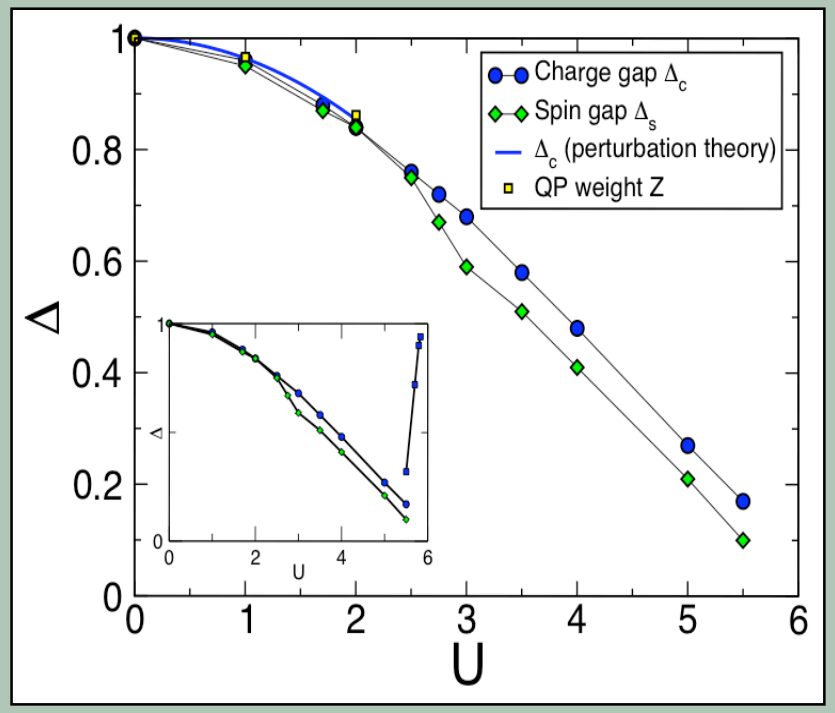


- charge gap reduced by interactions
- gap filled with incoherent excitations at high T
- band-insulator-like ρ at low T, bad metal ρ at high T
- local moment appears at high T





Spin and charge gaps as a function of U

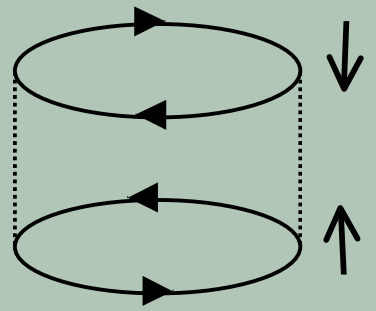


Spin gap is reduced compared to charge gap (at finite U).

Origin of charge gap renormalization:

$$\Delta_c = E(N+1) + E(N-1) - 2E(N)$$

$E^{(2)}$ =



$$E^{(2)} = -\frac{U^2}{L^3} \sum_{p_1,p_2,p_3,p_4} \frac{(1-n_{p_1\uparrow})n_{p_2\uparrow}(1-n_{p_3\downarrow})n_{p_4\downarrow}}{\epsilon_{p_1} - \epsilon_{p_2} + \epsilon_{p_3} - \epsilon_{p_4}}$$

$$\Delta_c = \Delta_c^0 \underbrace{\left[1 - 2U^2 \int_0^\infty d\lambda F^3(\lambda)\lambda \right]}_{\sim 1/W^2}$$

*Sentef, JK, Werner and Kampf PRB **80**, 155119 (2009)*

Summary

- LDA+DMFT can describe qualitatively different physics than LDA, such as PM phases of Mott insulators, quasiparticle renormalization, Kondo screening and heavy fermion physics

- Multiple bands can give raise to new phases and transitions not existing for simple models

Future and open problems

- Connection between LDA & DMFT - double-counting, calculation of interaction parameters cRPA, cLDA and charge self-consistency
- More efficient impurity solvers
- Linear response - spin, charge and orbital susceptibilites (dynamic)
- beyond single-site approximation: DCA, CDMFT, DΓA, dual fermions