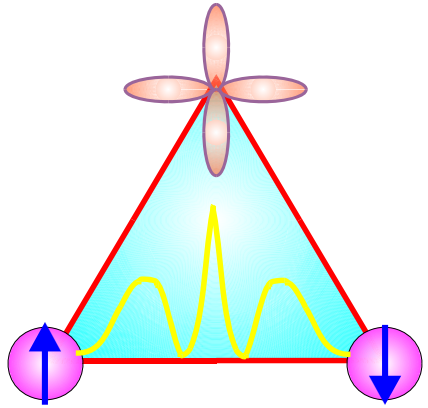


Spin and Orbital Fluctuations near Mott transitiosn: a cluster LDA+DMFT approach for 3d oxides

A. Lichtenstein

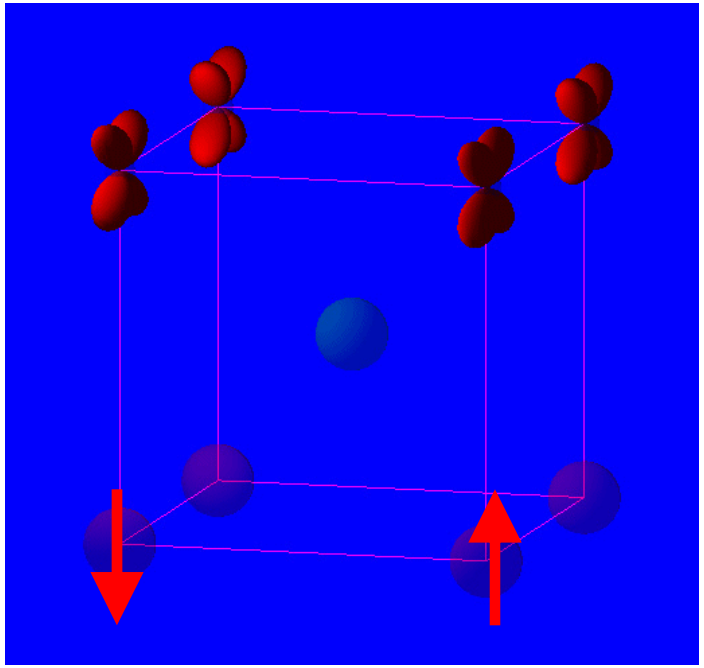
University of Hamburg

In collaborations with:

M. Katsnelson (Nijmegen), A. Rubtsov (Moscow)), G. Kotliar (Rutgers)
E. Gorelov, S. Brener and H. Hafermann (Hamburg)
A. Poteryaev, S. Biermann, A. Georges (EPL, Paris)
E. Pavarini, T. Saha-Dasgupta, O.K. Andersen (MPI-Stuttgart)

Outline

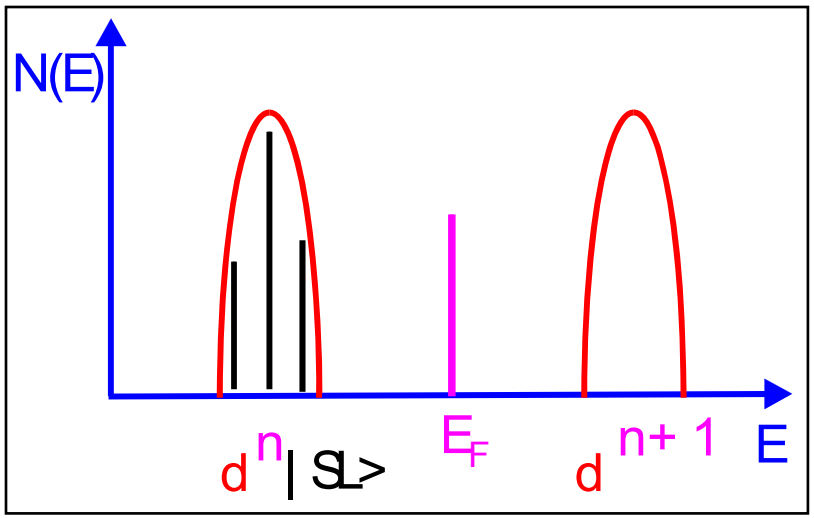
- Correlated systems: a cluster LDA+DMFT scheme
- Bonding vs. Correlation: MIT in TMO
- Beyond DMFT – nonlocal fluctuations
- Conclusions

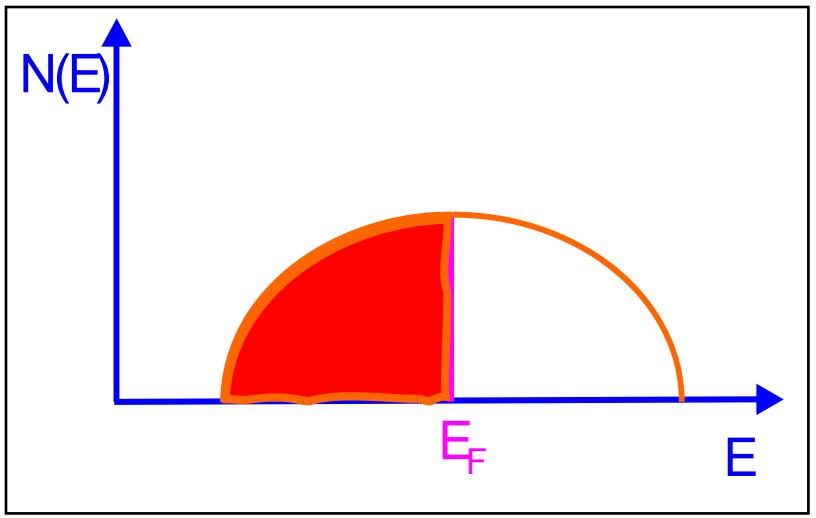


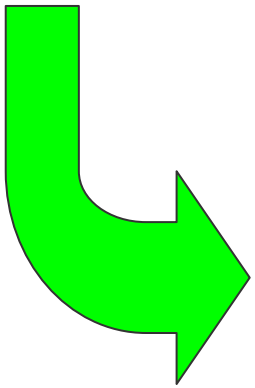
From Atom to Solid: DMFT

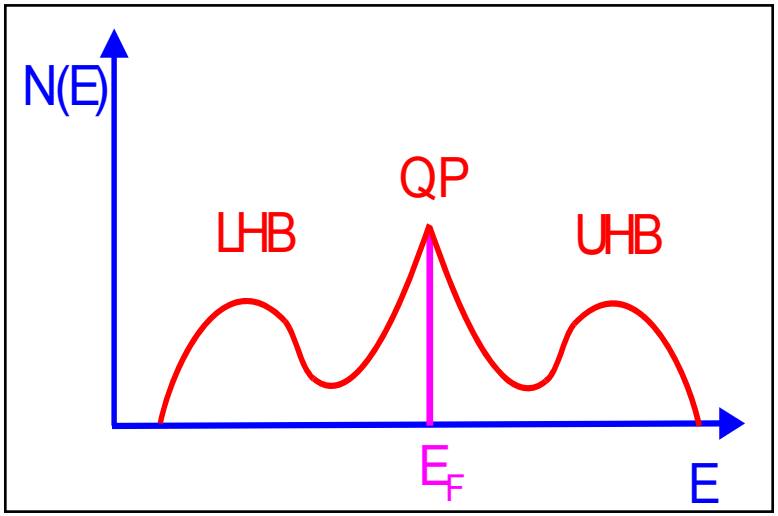
Atomic physics (U)

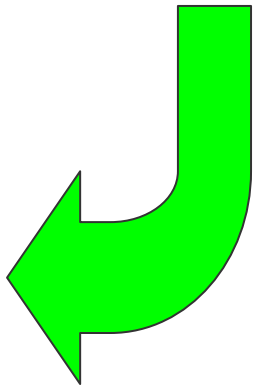
Bands effects (LDA)





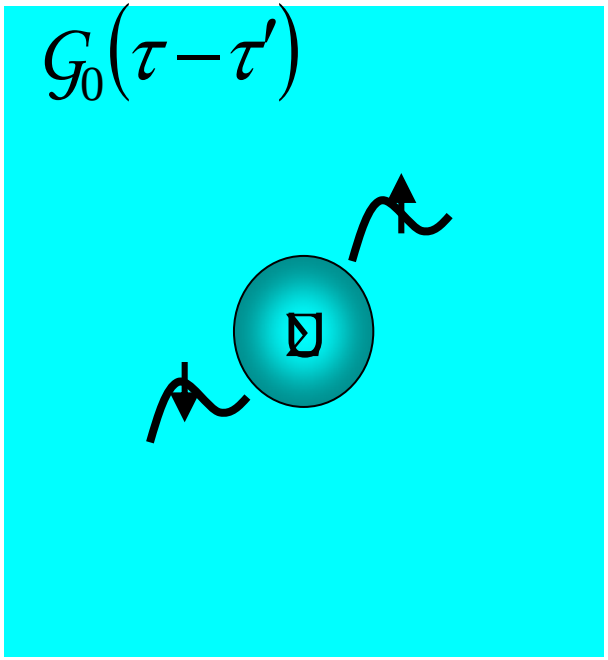






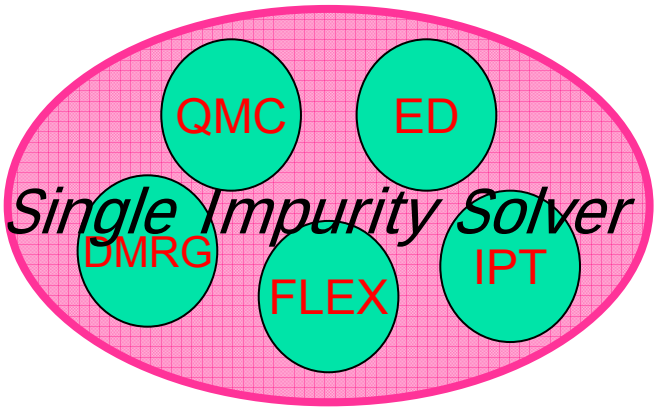
LDA+DMFT

DMFT: Self-Consistent Set of Equations



$$\hat{G}(i\omega_n)=\frac{1}{\Omega}\sum_{\vec{k}}^{BZ}\hat{G}(\vec{k},i\omega_n)$$

$$\hat{\mathcal{G}}_0^{-1}(i\omega_n)=\hat{G}^{-1}(i\omega_n)+\hat{\Sigma}(i\omega_n)$$



$$\hat{\Sigma}_{new}(i\omega_n)=\hat{\mathcal{G}}_0^{-1}(i\omega_n)-\hat{G}^{-1}(i\omega_n)$$

A. Georges and G. Kotliar (1992)
W. Metzner and D. Vollhardt (1987)

Real systems: LDA+cDMFT

V. Anisimov, et al. J. Phys. CM **9**, 7359 (1997)
A. Lichtenstein, et. al. PRB, **57**, 6884 (1998**)**

LDA+U
Static mean-field approximation
Energy-independent potential

$$\hat{V} = \sum_{mm'\sigma} |inlm\,\sigma > V^{\sigma}_{mm'} < inl\,m'\sigma|$$

Applications:
Insulators with long-range
spin-,orbital- and charge order

LDA+DMFT
Dynamic mean-field approximation
Energy-dependent self-energy operator

$$\hat{\Sigma}(\varepsilon) = \sum_{mm'\sigma} |inlm\sigma > \Sigma(\varepsilon)^{\sigma}_{mm'} < inlm'\sigma|$$

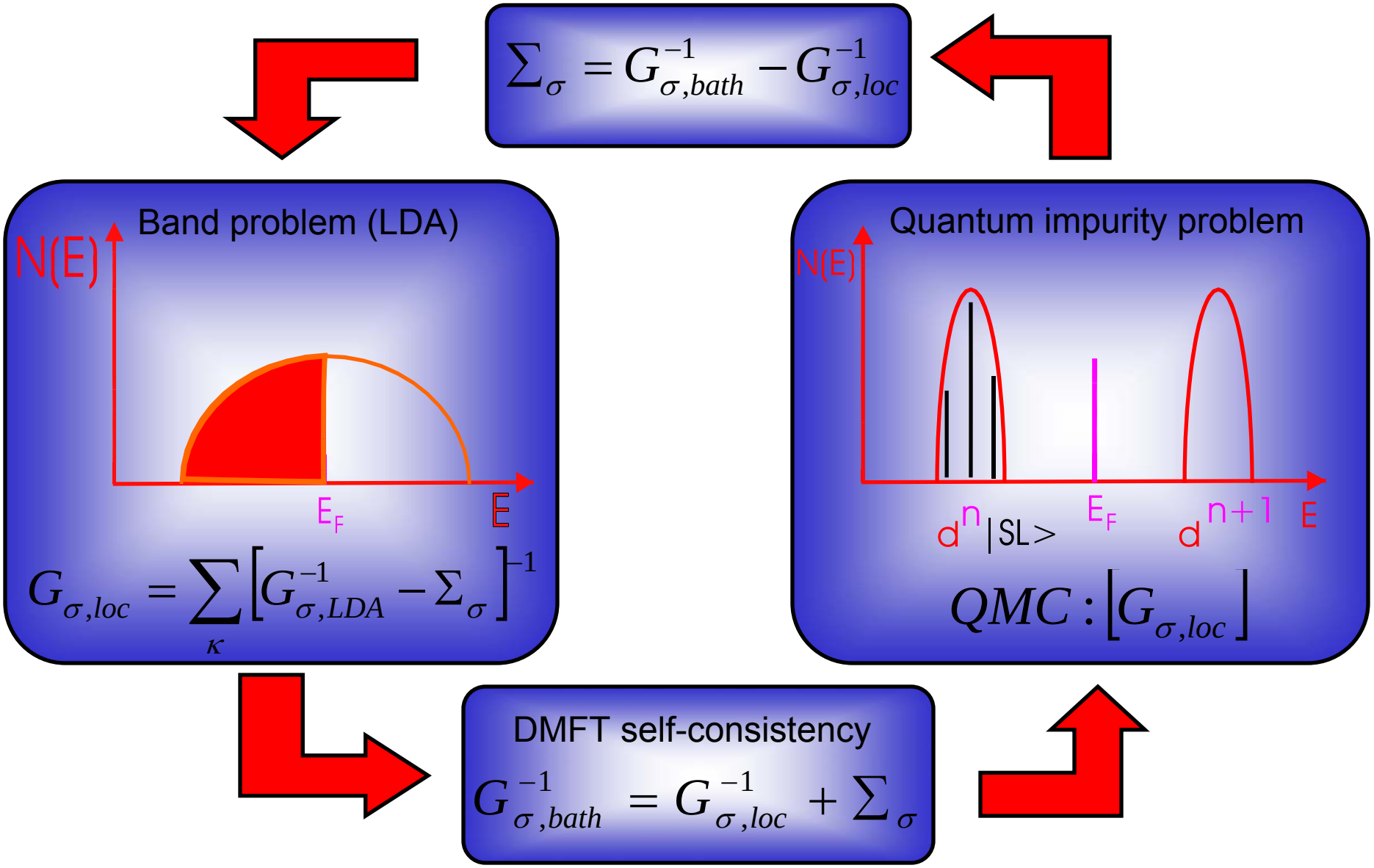
Applications:
Paramagnetic, paraorbital
strongly correlated metals

short range spin and orbital order

Cluster LDA+DMFT approximation

A. Poteryaev, A. Lichtenstein, and G. Kotliar, PRL **93**, 086401 (2004)
S. Biermann, A. Poteryaev, A. I. Lichtenstein, and A. Georges
Phys. Rev. Lett. 94, 026404 (2005)

Flow diagram for the LDA+cDMFT approach:

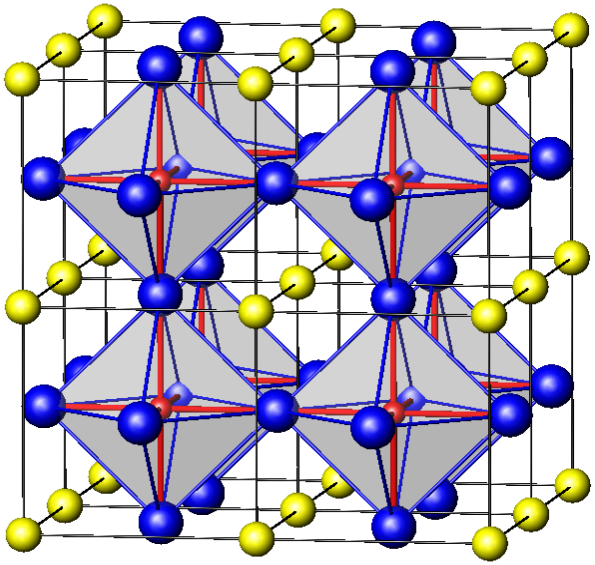


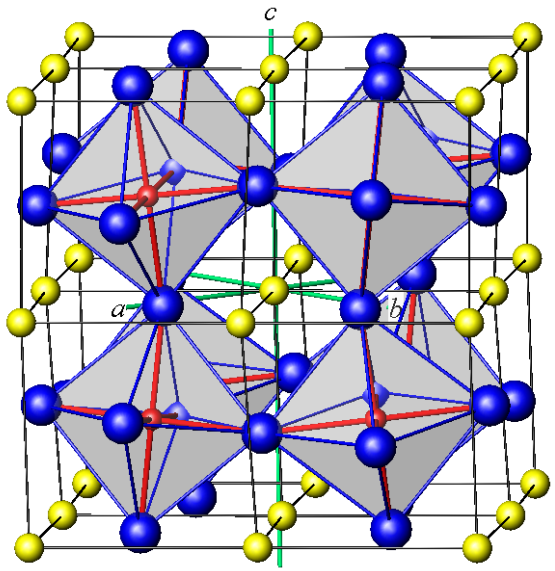
Orthorhombic $3d^1$ Perovskites

$SrVO_3$

Metal

m*/m=2.7





$CaVO_3$

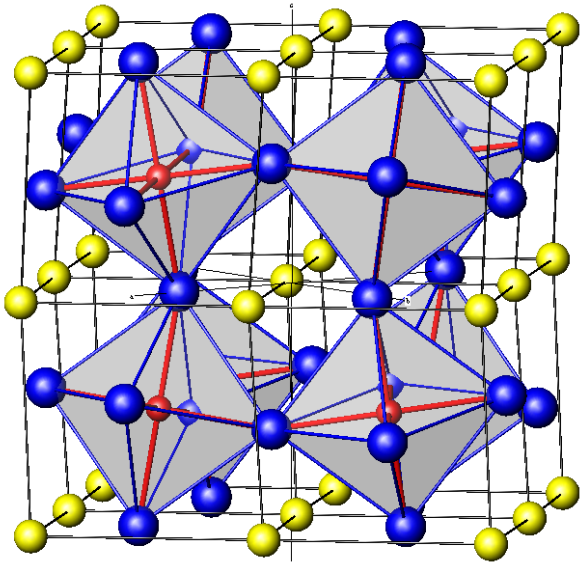
Metal

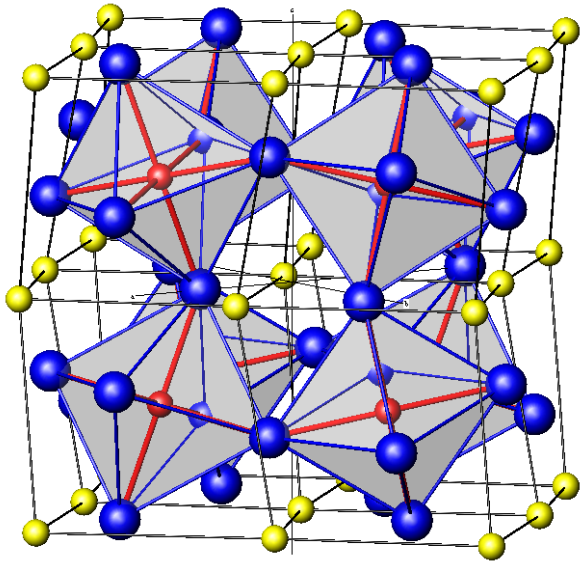
m*/m=3.6

$LaTiO_3$

Insulator

Gap=0.2eV



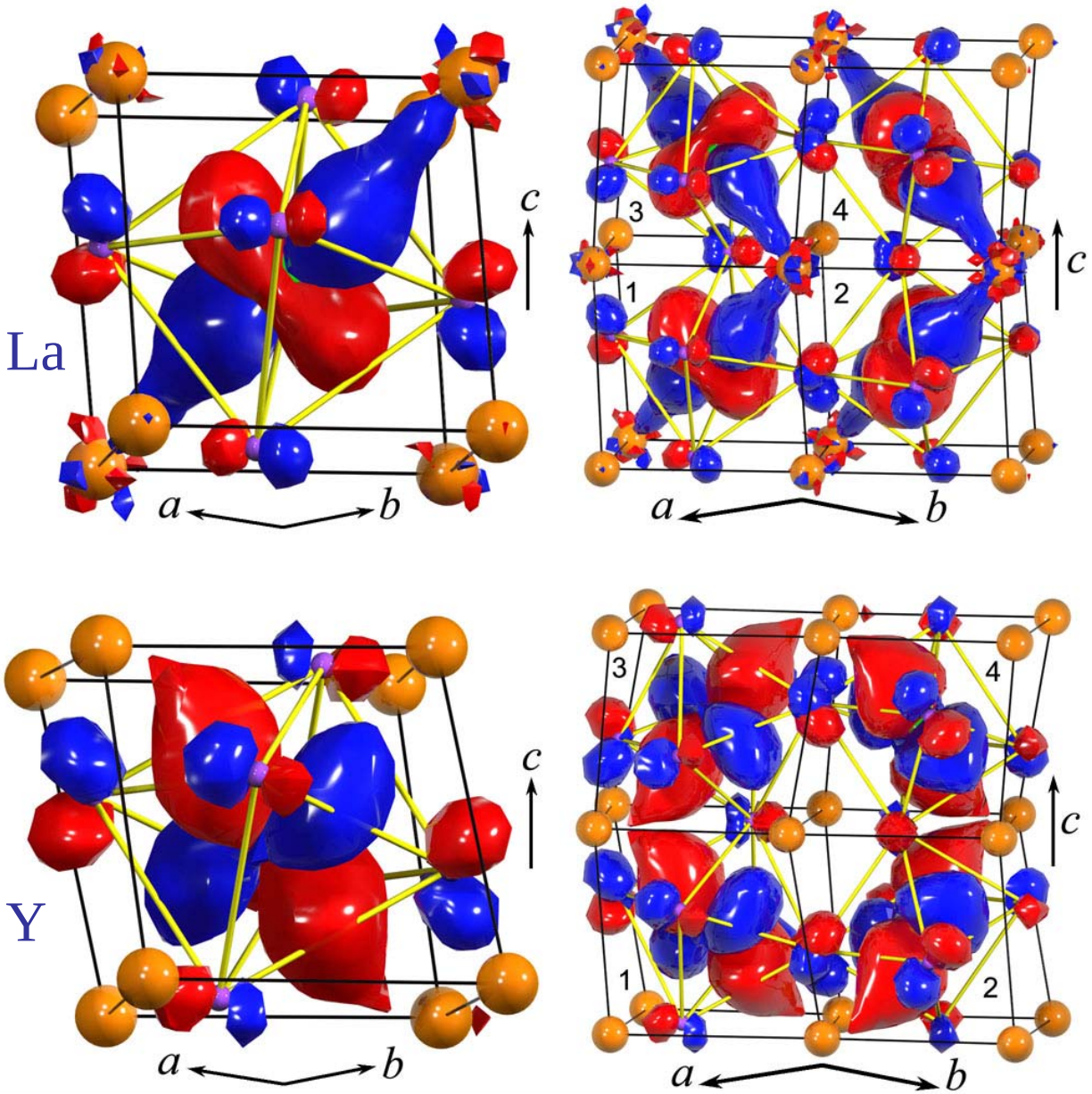


$YTiO_3$

Insulator

Gap=1.0eV

Orbital ordering in $MTiO_3$

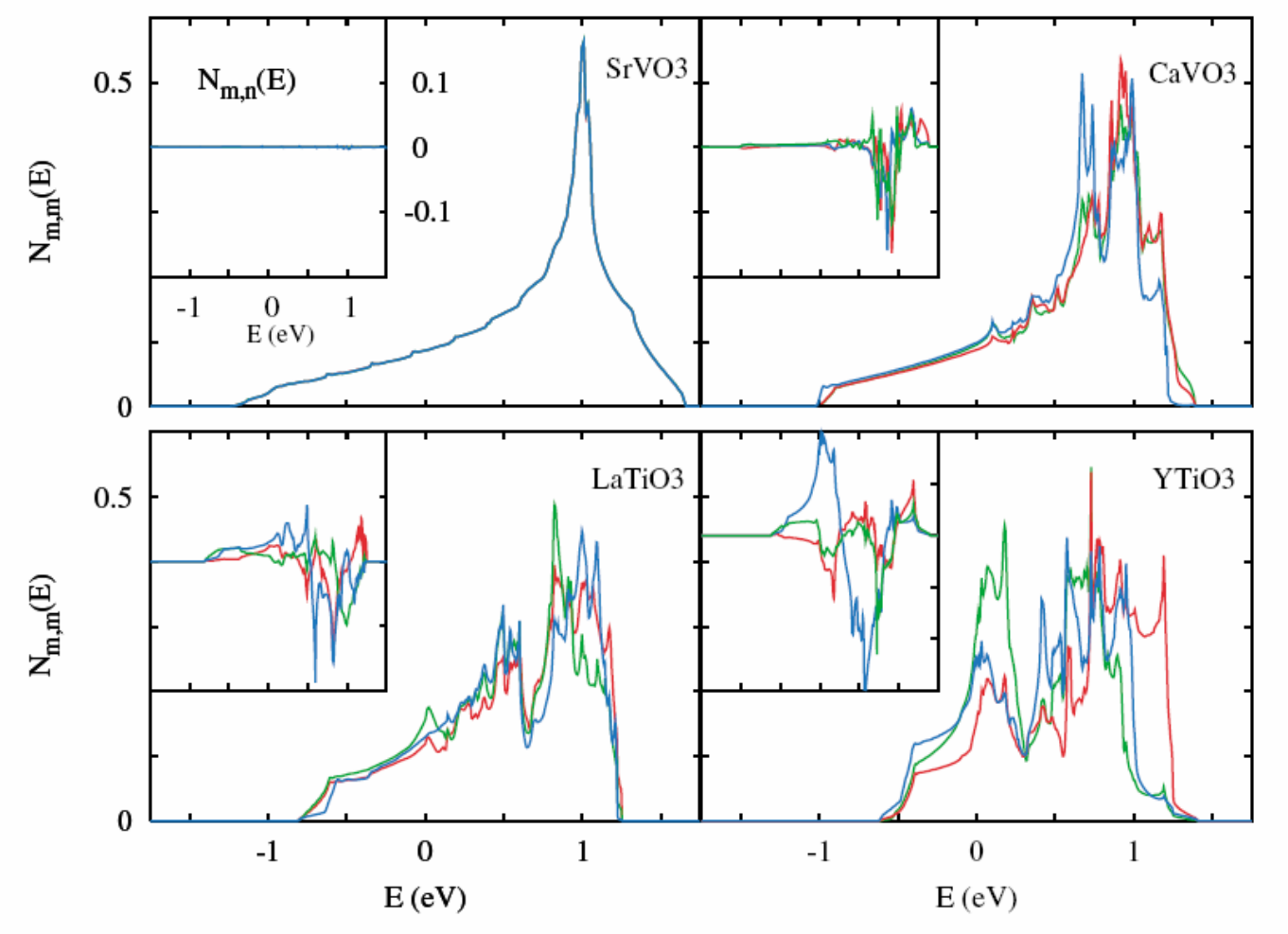


Violet: Oxygen
Orange: M

Occup.	LDA	**DMFT**
$LaTiO_3$	0.45	**0.88**
$YTiO_3$	0.50	**0.96**

E. Pavarini et al. PRL (2004)

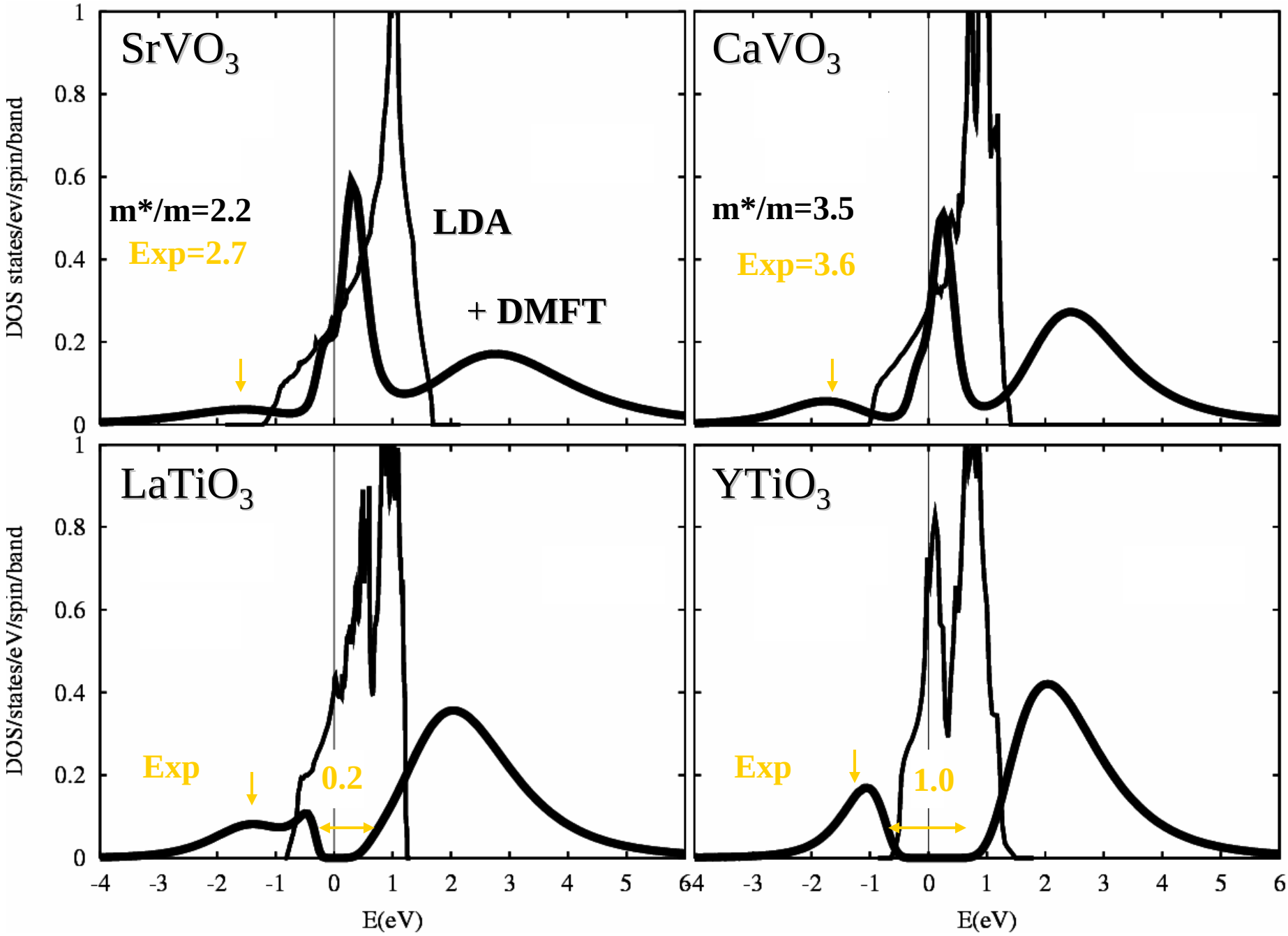
LDA-LMTO results: DOS



all metallic
in LDA

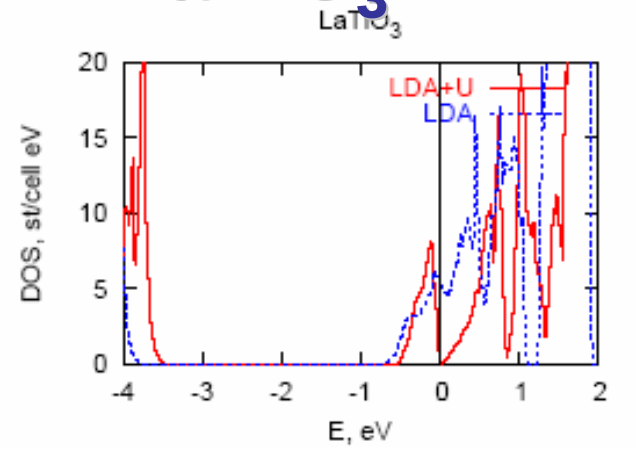
Crystal-field splittings w/in t_{2g} multiplet:
(140,200) meV for LaTiO3 ; (200,330) meV for YTiO3

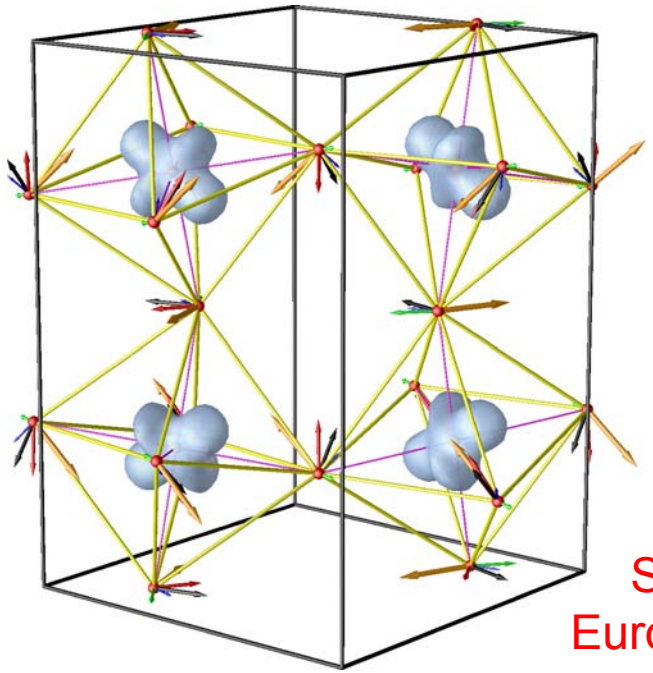
LDA+**DMFT:** comparison with **experiments**



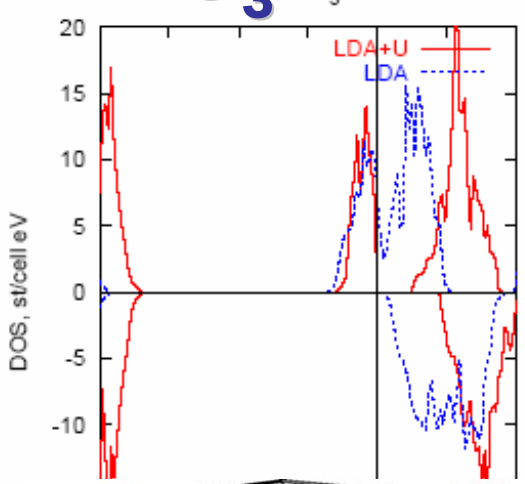
LDA+U : Forces and Orbital Ordering

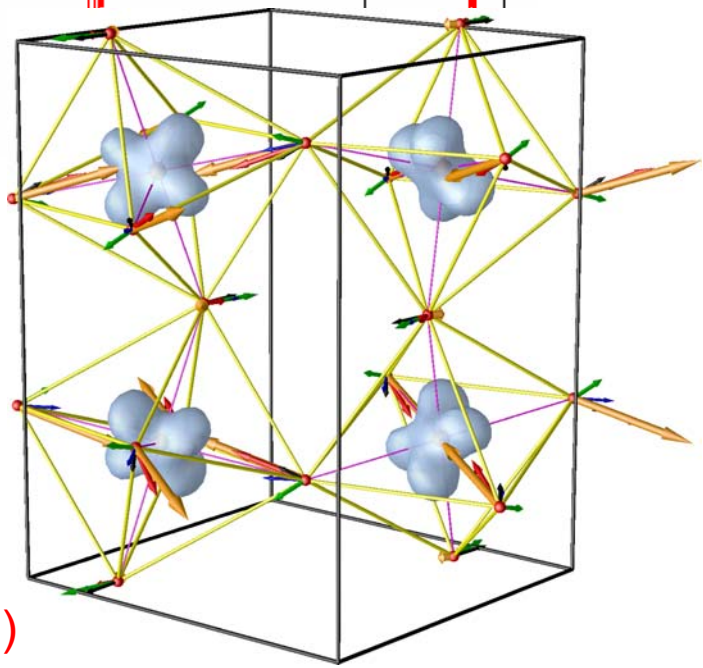
$LaTiO_3$ AFM





$YTiO_3$ FM

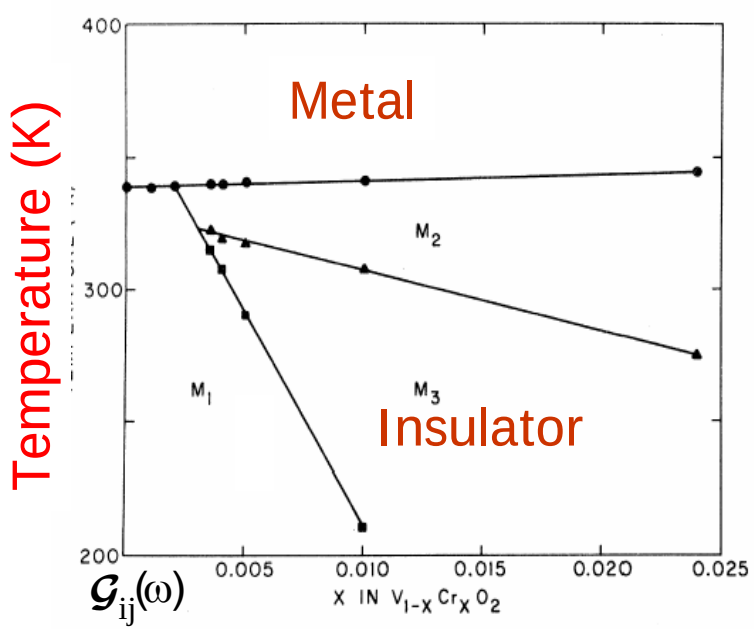


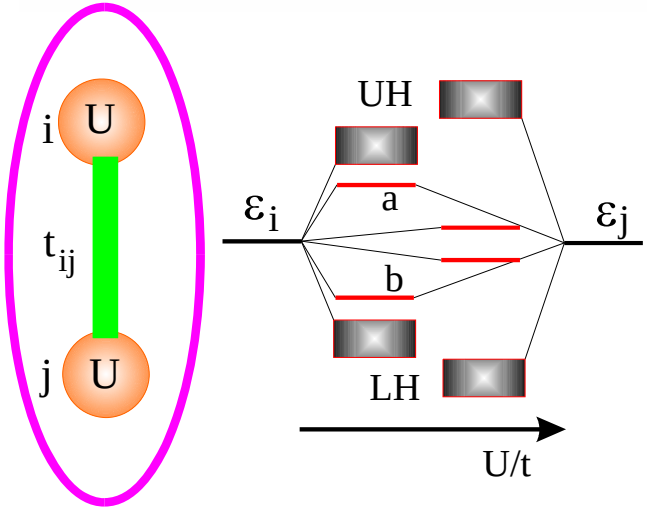


S. Okatov, et. al.
Europhys. Lett. (2004)

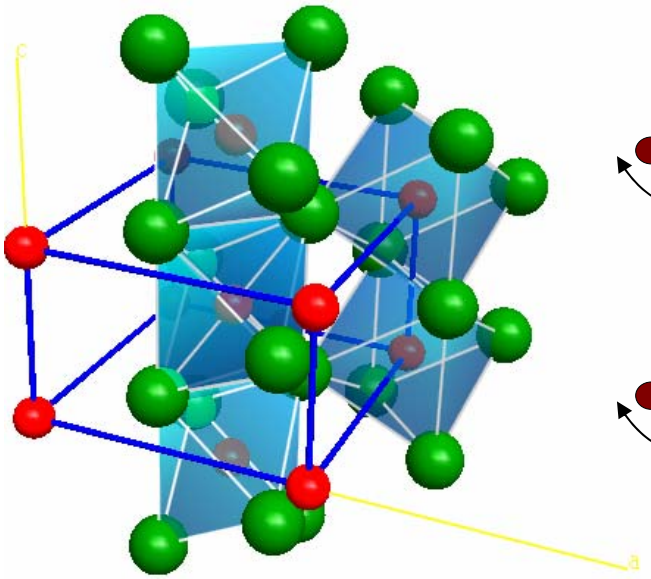
Phase diagram of VO_2: singlet formation

M. Marezio et al., (1972)

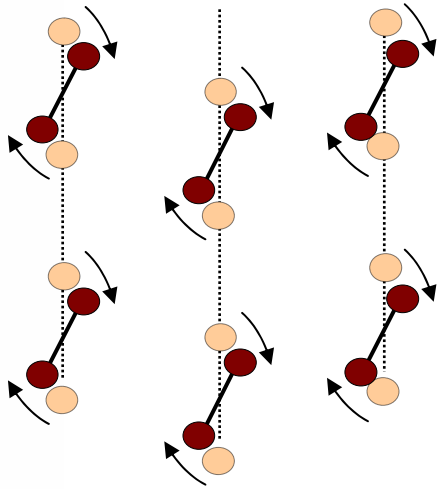




Rutile structure

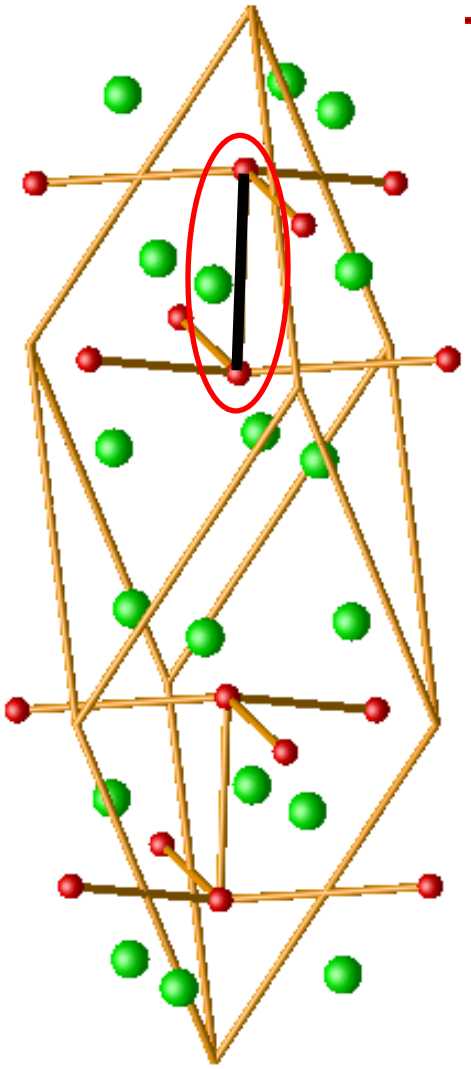


Monoclinic distortion in the insulating phase

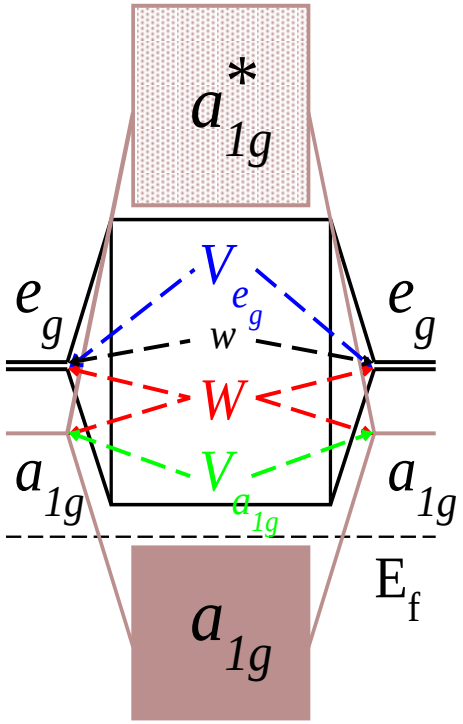


Correlation vs. Bonding

Intersite Coulomb interaction Ti_2O_3



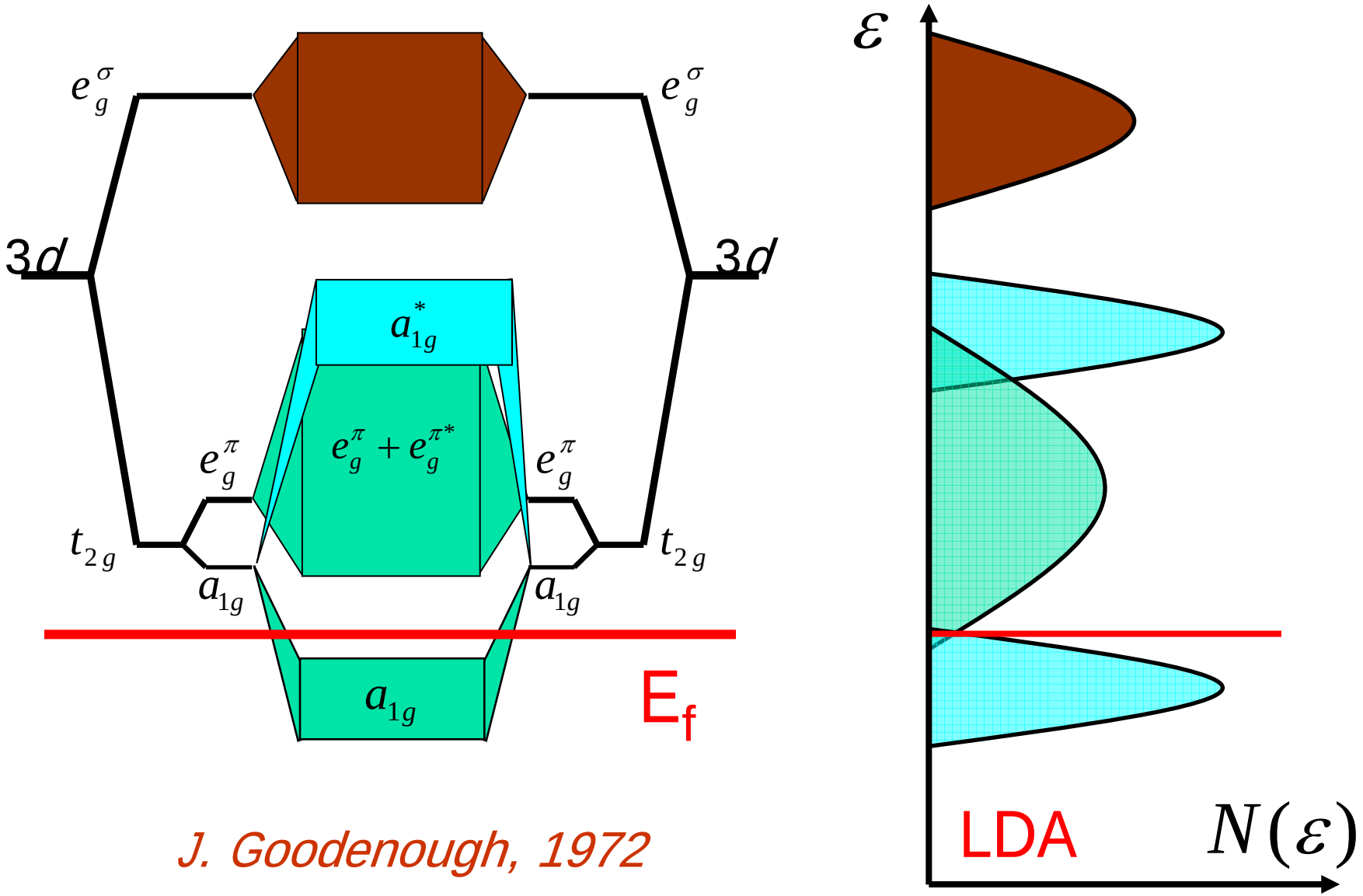
Corundum structure
for low and high temperature phases



Matrix of intersite Coulomb interaction

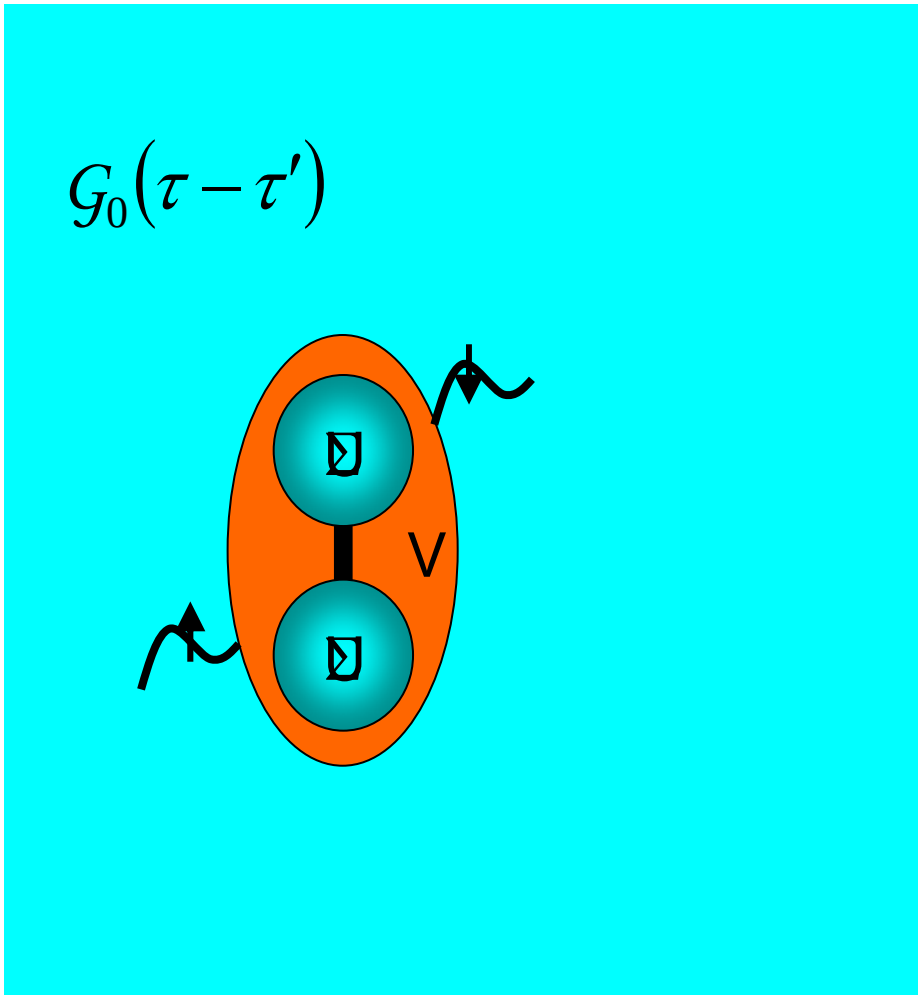
V_{eg}	w	W
w	V_{eg}	W
W	W	V_{a1g}

Electronic Structure



J. Goodenough, 1972

Cluster DMFT



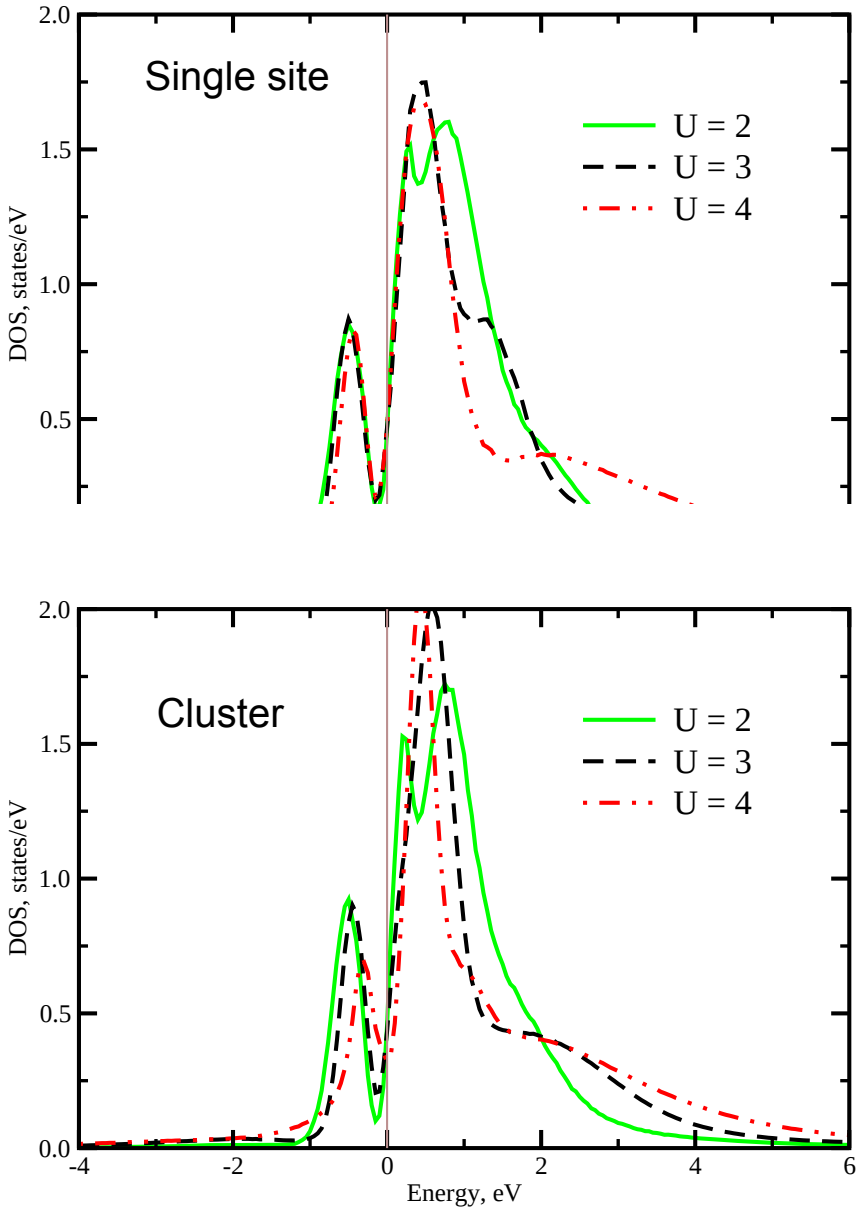
M. Hettler et al, PRB 58, 7475 (1998)
A. Lichtenstein, et al, PRB 62, R9283 (2000)
G. Kotliar, et al, PRL 87, 186401 (2001)

Local Green function

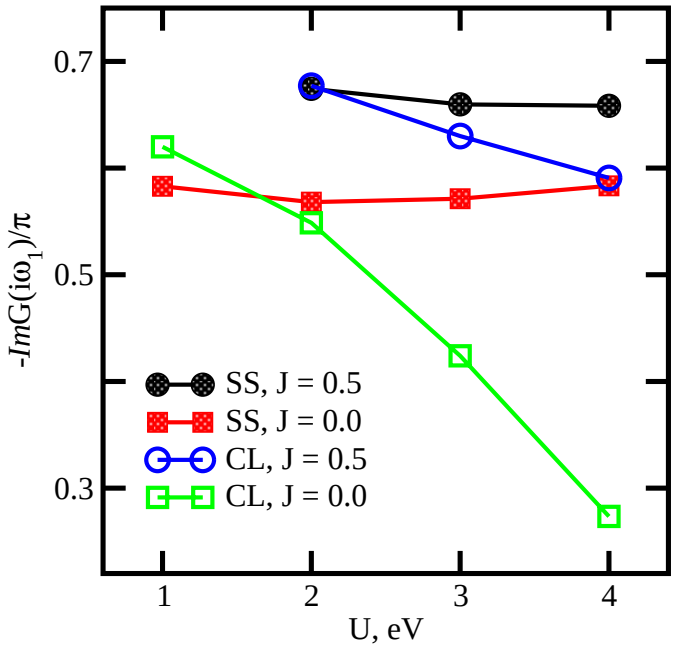
$$\hat{G}^{-1}(\mathbf{k}, i\omega_n) = (i\omega_n + \mu)\hat{I} - \hat{H}(\mathbf{k}, i\omega_n)$$

$$\hat{H}(\mathbf{k}, i\omega_n) = \left(\begin{array}{cc|cc} \hat{H}_{11} + \hat{\Sigma}_{11} & \hat{H}_{12} + \hat{\Sigma}_{12} & \hat{H}_{13} & \hat{H}_{14} \\ \hat{H}_{21} + \hat{\Sigma}_{21} & \hat{H}_{22} + \hat{\Sigma}_{22} & \hat{H}_{23} & \hat{H}_{24} \\ \hline \hat{H}_{31} & \hat{H}_{32} & \hat{H}_{33} + \hat{\Sigma}_{11} & \hat{H}_{34} + \hat{\Sigma}_{12} \\ \hat{H}_{41} & \hat{H}_{42} & \hat{H}_{43} + \hat{\Sigma}_{21} & \hat{H}_{44} + \hat{\Sigma}_{22} \end{array}\right)$$

Single site and cluster DMFT without intersite Coulomb



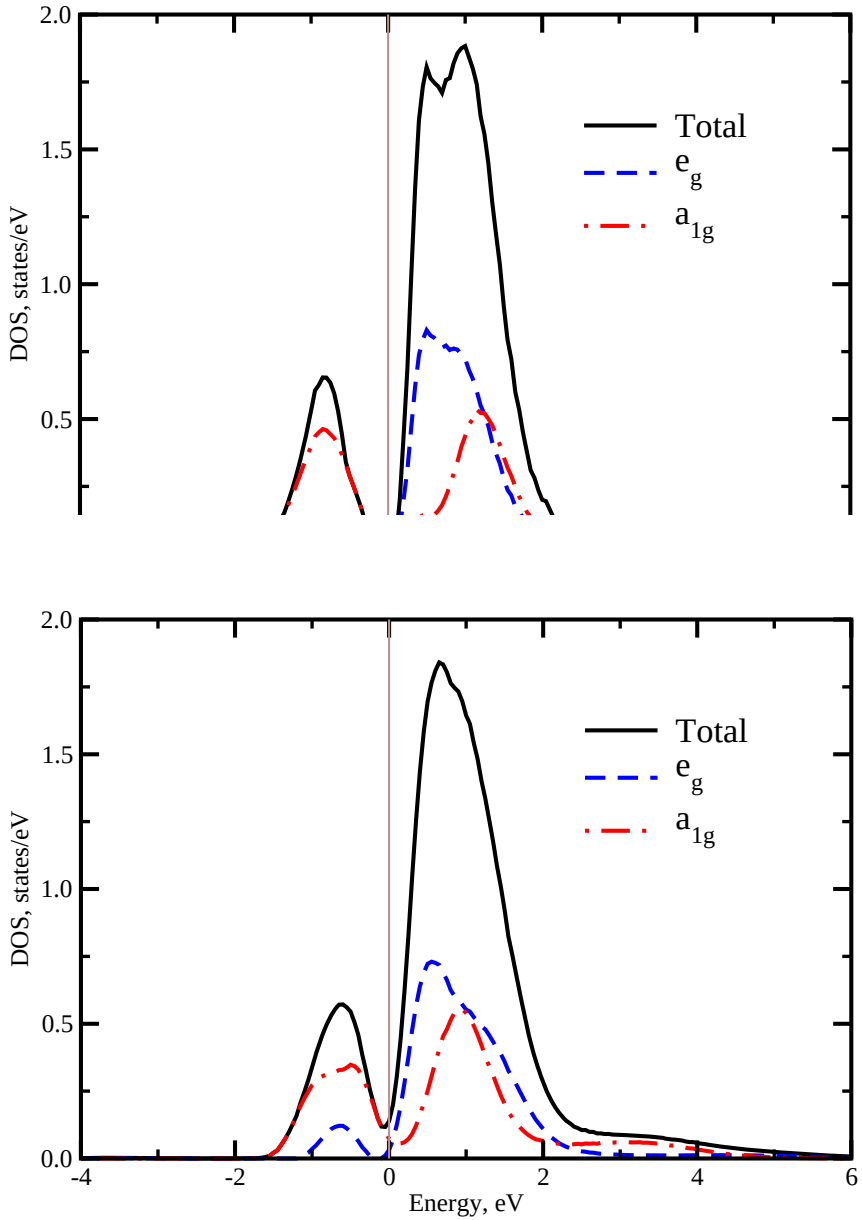
Total number of states
at first Matsubara point



- Metallic solutions in single site and cluster DMFT without intersite Coulomb interaction

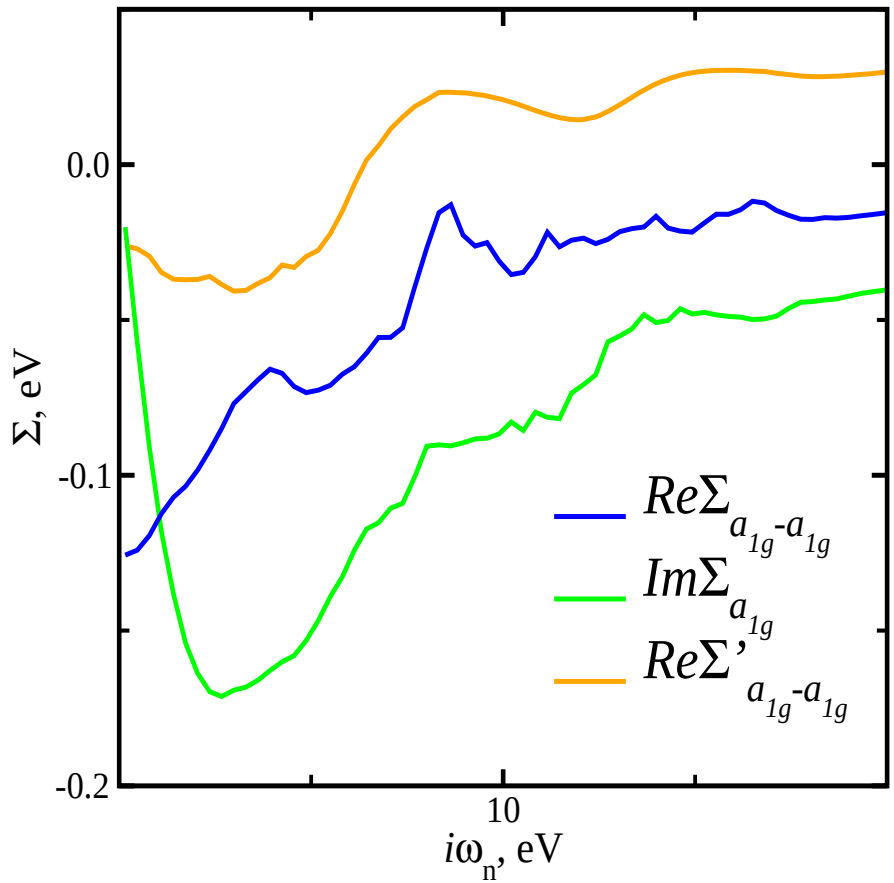
- Needs a big value of Coulomb parameter *U* in order to obtain insulator

Cluster LDA+DMFT w



U =

β =

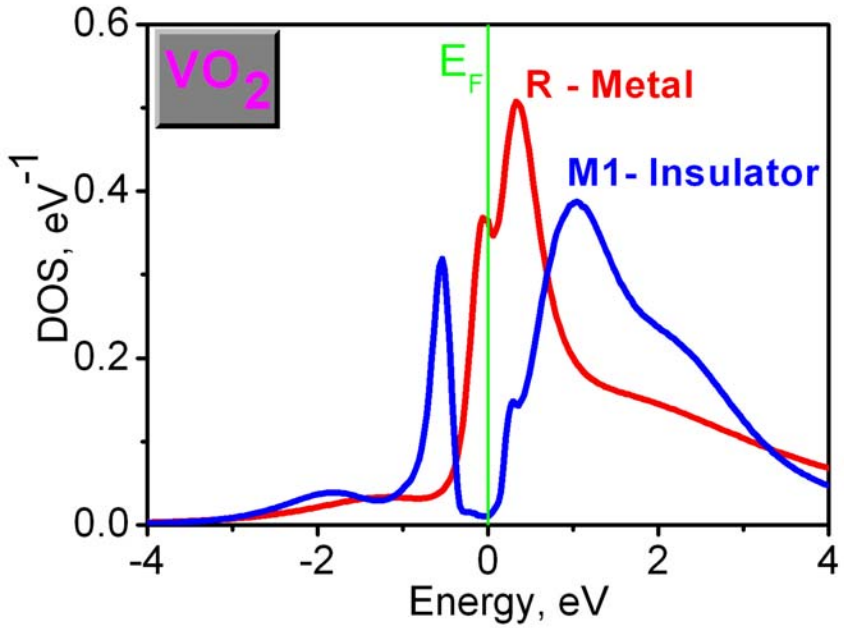


A. Poteryaev, et al, PRL**93**, 086401 (2004)

U = 2, δ = 0.5, W = 0.5

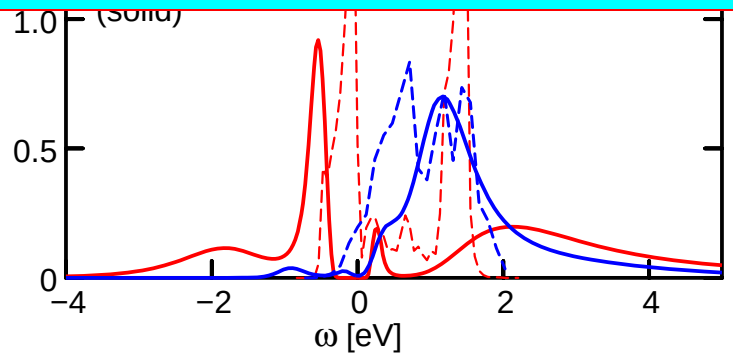
β = 10 eV^{-1}, HT structure

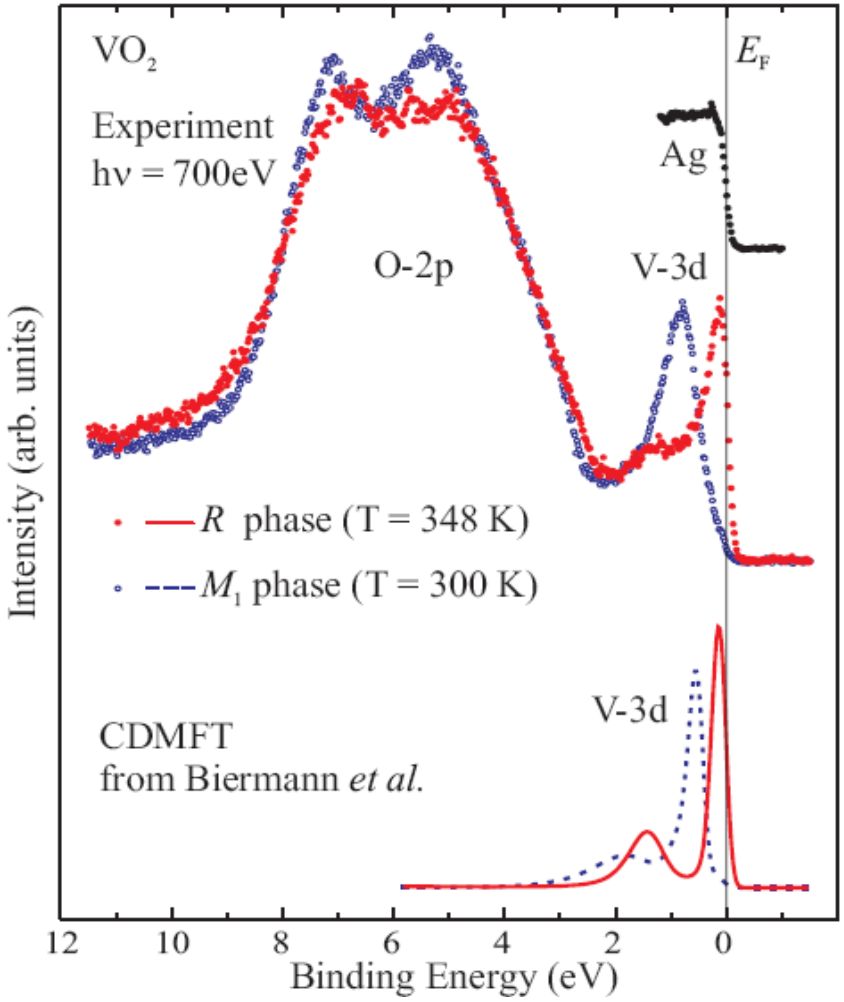
Cluster-DMFT results for VO_2



M1

Sharp peak below the gap is NOT a Hubbard band !

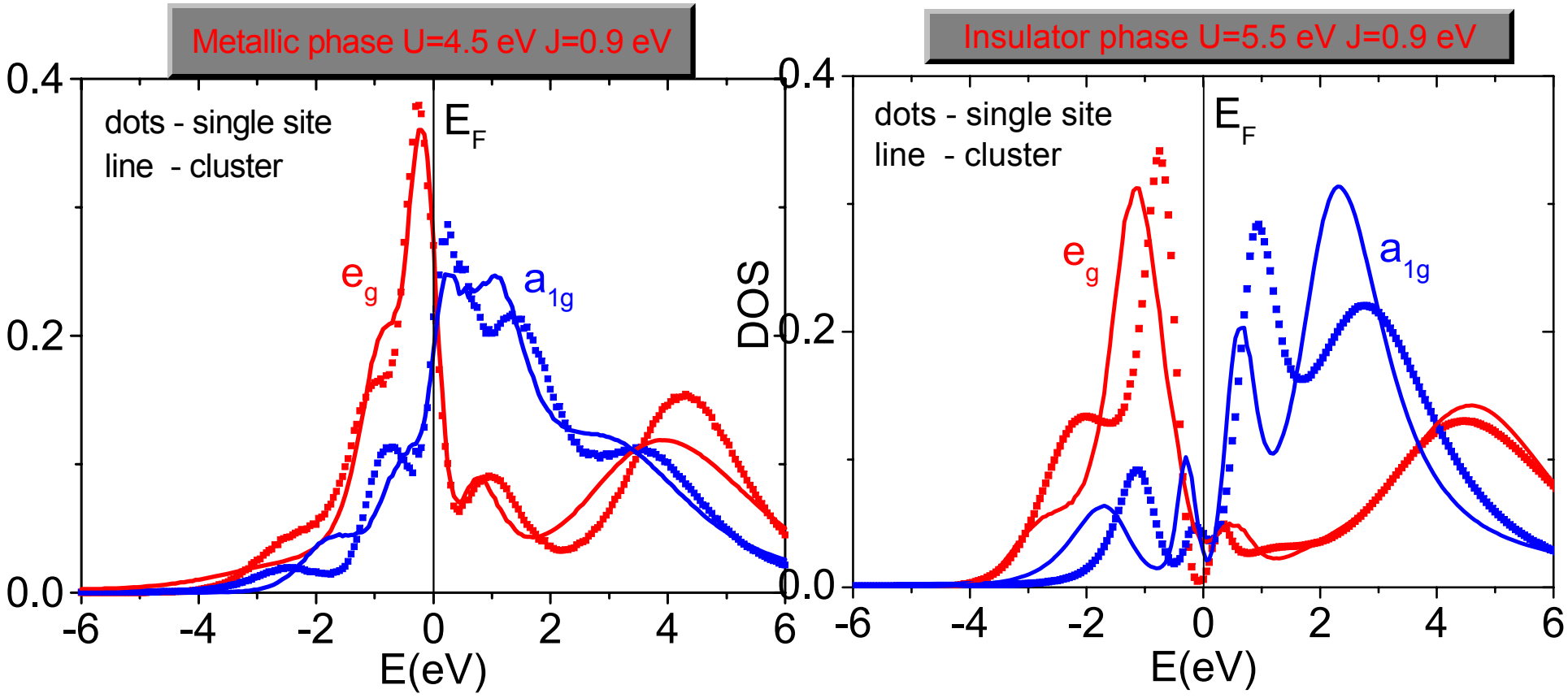




New photoemission from Tjeng's group
T. C. Koethe, et al. PRL (2006)

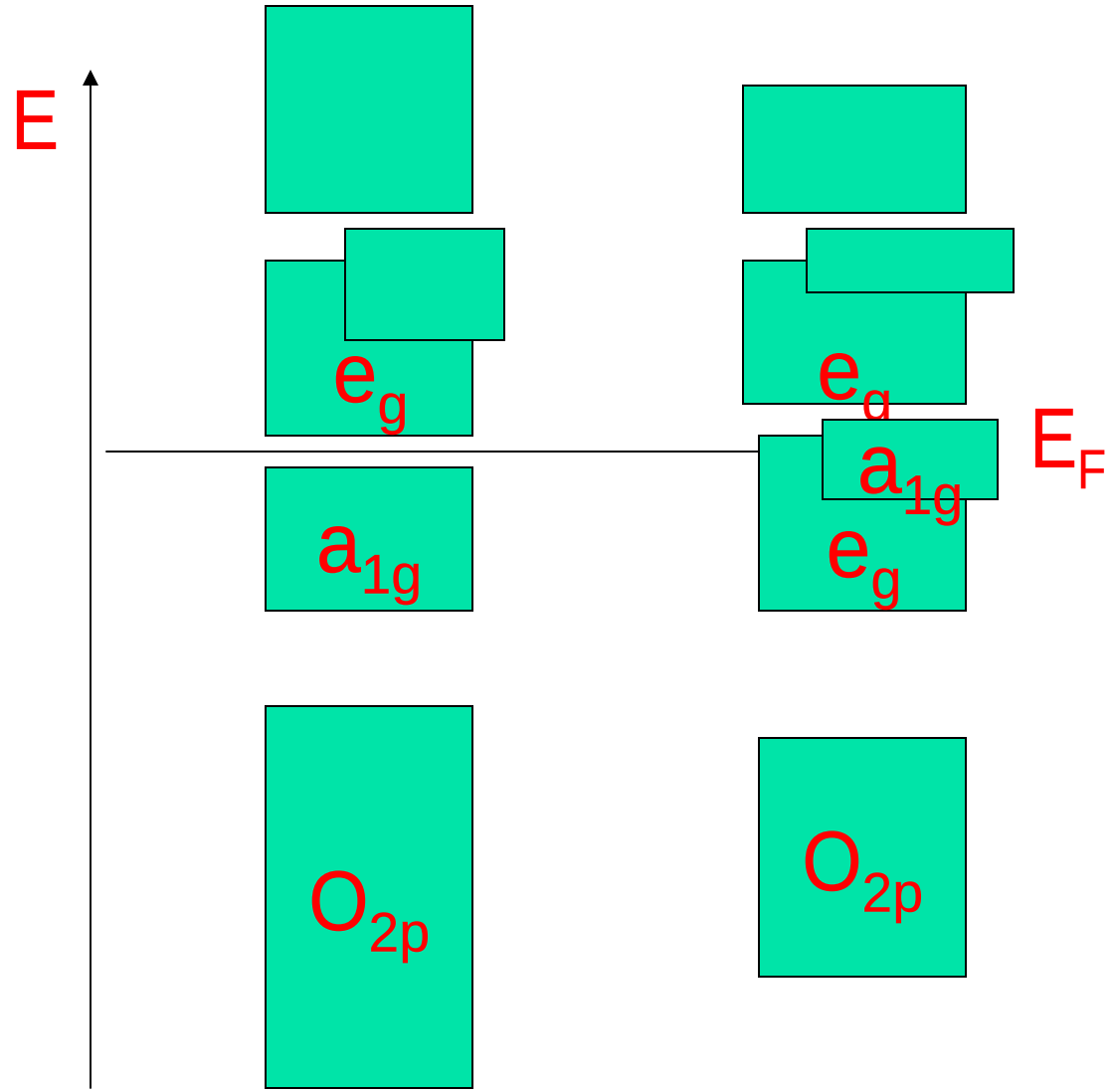
S. Biermann, et al, PRL **94**, 026404 (2005)

d^2-case: Cluster DMFT for V_2O_3



(A. Poteryaev et al, unpublished)

J. Goodenough diagram



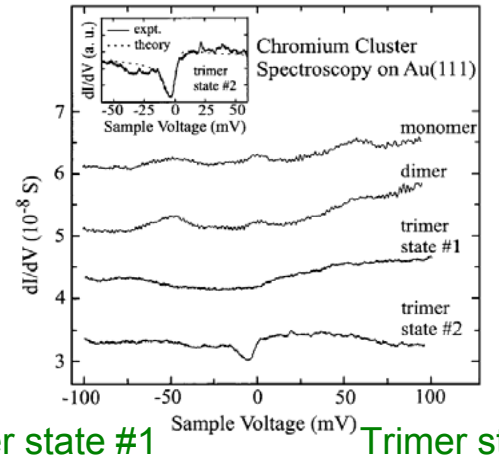
d^2 is more localized then d^1 due to Hund's rule coupling – J
Therefore single site DMFT works better for V_2O_3 then for Ti_2O_3

Magnetic nanoclusters on surface

Experiment

A single antiferromagnetic chromium trimer on gold surface:
M. Crommie Phys. Rev. Lett. **87**, 256804 (2001)

STM *dI/dV* spectra



Trimer state #1 Trimer state #2

Kondo resonance is observed for isosceles trimer (state #2)

Theory

Interplay between single-impurity Kondo effect and RKKY exchange

↓

Complicated phase diagram

↓

Quantum critical points

Heavy fermions

Non-Fermi-liquid behavior

↓

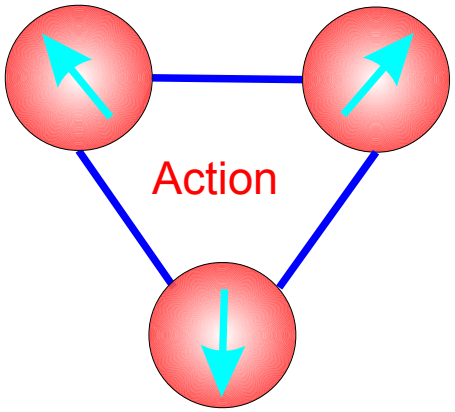
Uncontrollable approximations:

Replacement of Heisenberg exchange by Ising one

Model: correlated exchange-triangle

a) Is the difference between Heisenberg and Ising types of the exchange interaction essential?

b) How does geometry of the problem affect on Kondo response of the system?



Bath Green function

$$S = S_0 + W$$

$$S_0 = -\int_0^\beta \int_0^\beta d\tau d\tau' \sum_{i,j;\sigma} c^\dagger_{i\sigma}(\tau)\mathcal{G}^{-1}_{ij}(\tau-\tau')c_{j\sigma}(\tau')$$

$$W = \int_0^\beta d\tau \left(U \sum_i n_{i\uparrow}(\tau)n_{i\downarrow}(\tau) + \sum_{i,j} J_{ij}\mathbf{S}_i(\tau)\mathbf{S}_j(\tau) \right)$$

$$\mathcal{G}^{-1}_{ij} = \mathcal{G}^{-1}_{i}\delta_{ij} - t_{ij}$$

$$\mathcal{G}^{-1}_{i}(i\omega_n) = \mu + i(\omega_n + \sqrt{\omega_n^2 + 1})/2$$

Interaction W

First term – Hubbard repulsion

Second term – intersite exchange interaction

Continuous Time QMC formalism

Formal perturbation-series:

$$Z = \sum_{k=0}^{\infty} \int dr_1 \int dr'_1 \ldots \int dr_{2k} \int dr'_{2k} \Omega_k (r_1, r'_1, \ldots, r_{2k}, r'_{2k})$$

$$\Omega_k (r_1, r'_1, \ldots, r_{2k}, r'_{2k}) = Z_0 \frac{(-1)^k}{k!} w^{r'_1 r'_2}_{r_1 r_2} \ldots w^{r'_{2k-1} r'_{2k}}_{r_{2k-1} r_{2k}} D^{r_1 \ldots r_{2k}}_{r'_1 \ldots r'_{2k}}$$

$$D^{r_1 \ldots r_{2k}}_{r'_1 \ldots r'_{2k}} = \left\langle T \left(c^+_{r'_1} c^{r_1} - \alpha^{r_1}_{r'_1} \right) \ldots \left(c^+_{r'_{2k}} c^{r_{2k}} - \alpha^{r_{2k}}_{r'_{2k}} \right) \right\rangle$$

Since S_0 is Gaussian one can apply the Wick theorem → *D* can be presented as a determinant g0

The Green function can be calculated as follows

$$g^r_{r'}(k) = \frac{\left\langle T c^+_{r'} c^r \left(c^+_{r'_1} c^{r_1} - \alpha^{r_1}_{r'_1} \right) \ldots \left(c^+_{r'_{2k}} c^{r_{2k}} - \alpha^{r_{2k}}_{r'_{2k}} \right) \right\rangle}{\left\langle T \left(c^+_{r'_1} c^{r_1} - \alpha^{r_1}_{r'_1} \right) \ldots \left(c^+_{r'_{2k}} c^{r_{2k}} - \alpha^{r_{2k}}_{r'_{2k}} \right) \right\rangle}$$

ratio of determinants → In practice efficient calculation of a ratio is possible due to fast-update formulas

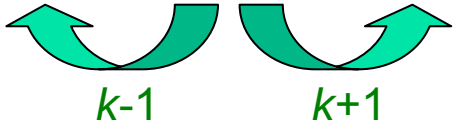
A. Rubtsov and A.L., JETP Lett. 80, 61 (2004)

Random walks in the space of Ω_k

One can perform a random walks over terms of the partition function expansion to calculate multidimensional integrals and thus the partition function itself

$$Z = \sum_{k=0}^{\infty} \Omega_k$$

$$Z = \ldots + \Omega_{k-1} + \Omega_k + \Omega_{k+1} + \ldots$$



Acceptance ratio

Step k-1

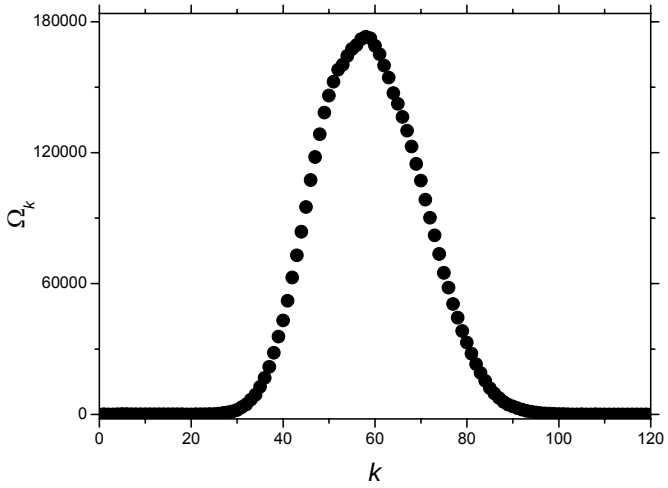
$$\frac{k}{|w|}\frac{D^{k-1}}{D^k}$$

Step k+1

$$\frac{|w|}{k+1}\frac{D^{k+1}}{D^k}$$

$$\Omega_k \sim \int dr_1 \int dr'_1 \ldots \int dr_{2k} \int dr'_{2k}$$

An example of Ω_k distribution



The sign problem

Average sign depends on the choice of parameters $\alpha^r_{r'}$

For Hubbard model at half-filling average sign is 1 if these parameters are constants and the following conditions are fulfilled:

For Hubbard model with attraction $\alpha_\uparrow = \alpha_\downarrow = \alpha$

For Hubbard model with repulsion $\alpha_\uparrow + \alpha_\downarrow = 1$

Miracle of CT-QMC: super-perturbation

$$S=\sum_{\sigma\sigma'}\int_0^\beta d\tau\int_0^\beta d\tau[-G_0^{-1}(\tau-\tau')c_\sigma^+(\tau)c_\sigma(\tau')+\frac{1}{2}U\delta(\tau-\tau')c_\sigma^+(\tau)c_{\sigma'}^+(\tau)c_{\sigma'}(\tau)c_\sigma(\tau)]$$

$$G_0^{-1}(\tau-\tau')=\delta(\tau-\tau')[\frac{\partial}{\partial\tau}+\mu]-\Delta(\tau-\tau')$$

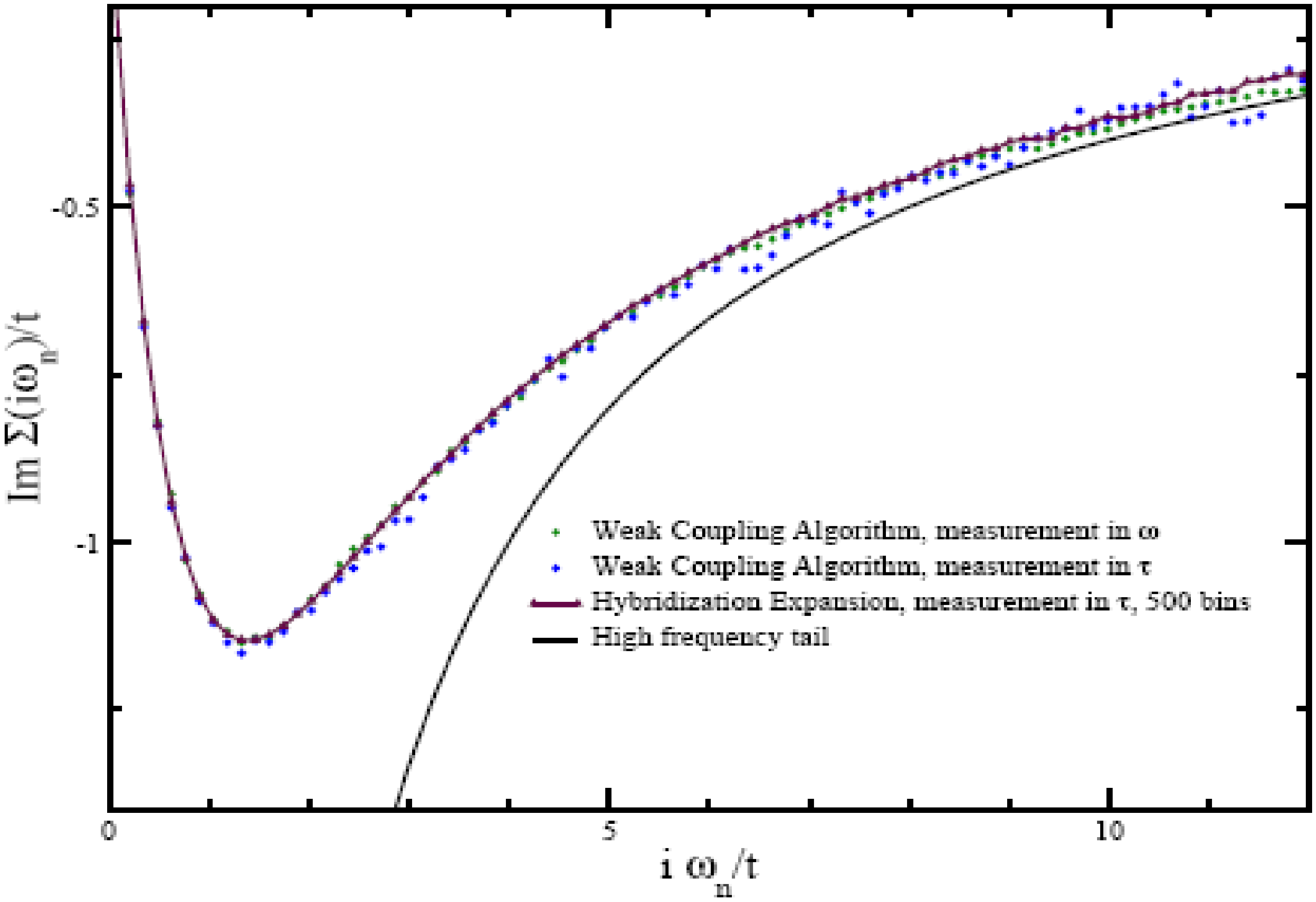
Weak coupling expansion (A. Rubtsov et. al)

$$Z=\sum_{k=0}^{\infty}\frac{(-U)^k}{k!}\det[G_0(\tau-\tau')]$$

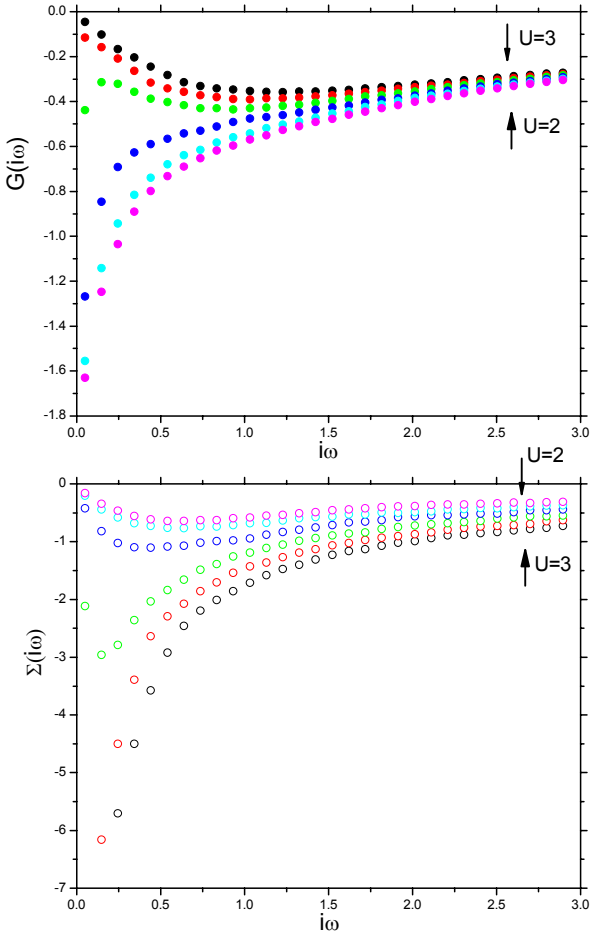
Strong coupling expansion (P. Werner et. al)

$$Z=\sum_{k=0}^{\infty}\frac{1}{k!}Tr\left\langle c_\sigma^+(\tau)c_\sigma(\tau')...c_{\sigma'}^+(\tau)c_{\sigma'}(\tau')\right\rangle_{loc}\det[\Delta(\tau-\tau')]$$

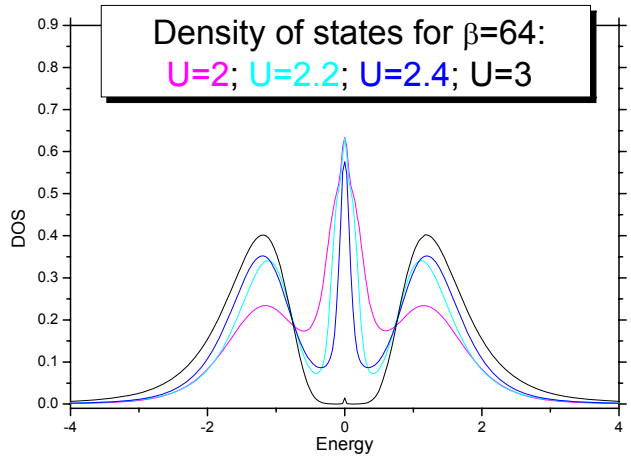
Comparisson of different CT-QMC: U=W

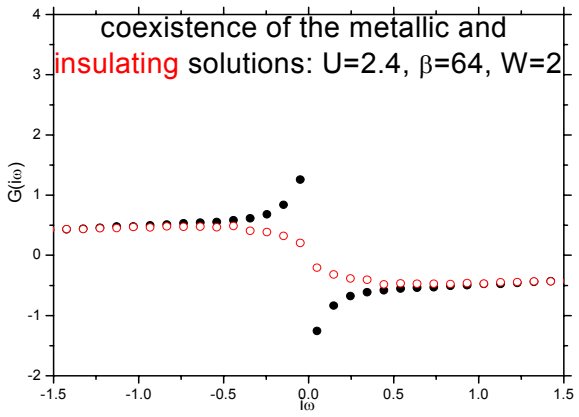


Metal-insulator transition in the Hubbard model on Bethe lattice



DMFT on Bethe lattice. Parameters:
U=2, U=2.2, U=2.4, U=2.6, U=2.8, U=3
β=64, band width W=2





CTQMC scheme with β=64

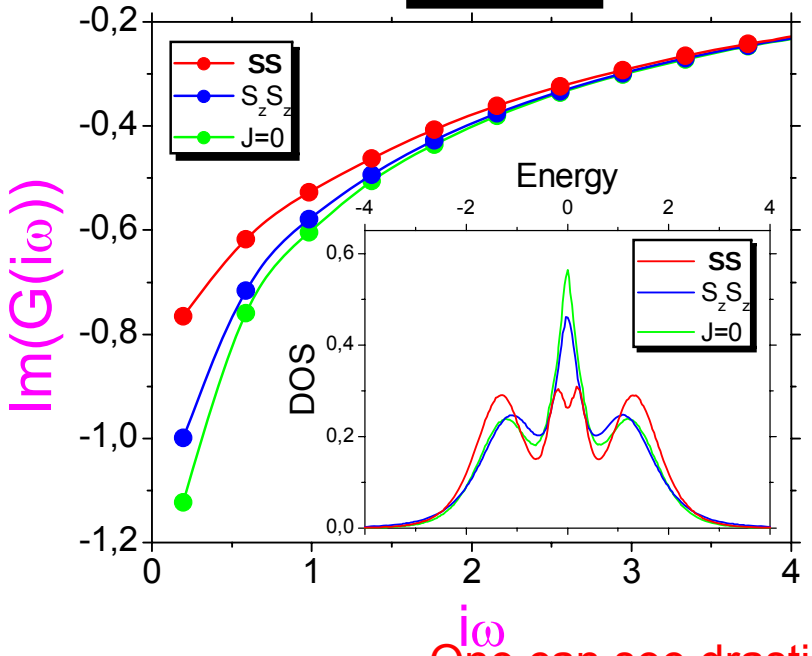
Heisenberg vs. Ising exchange

Intersite exchange term can have Heisenberg (**SS**) or Ising (S_zS_z) form

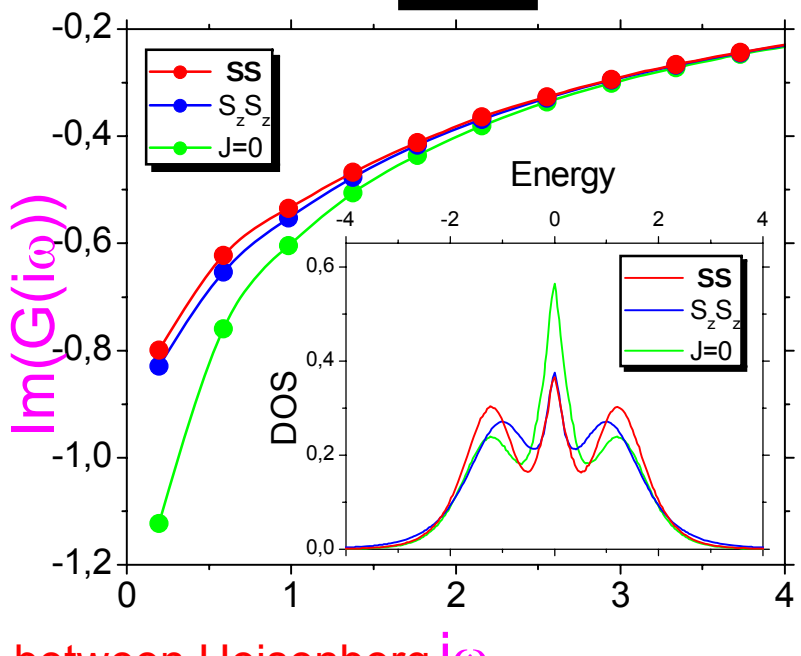
Exchange integral J can be antiferromagnetic (AFM, $J>0$) or ferromagnetic (FM, $J<0$)

U=2, J=+-0.2, t=0, β=16, $\mu=U/2$

AFM



FM



One can see drastic difference between Heisenberg and Ising types of interaction for antiferromagnetic case

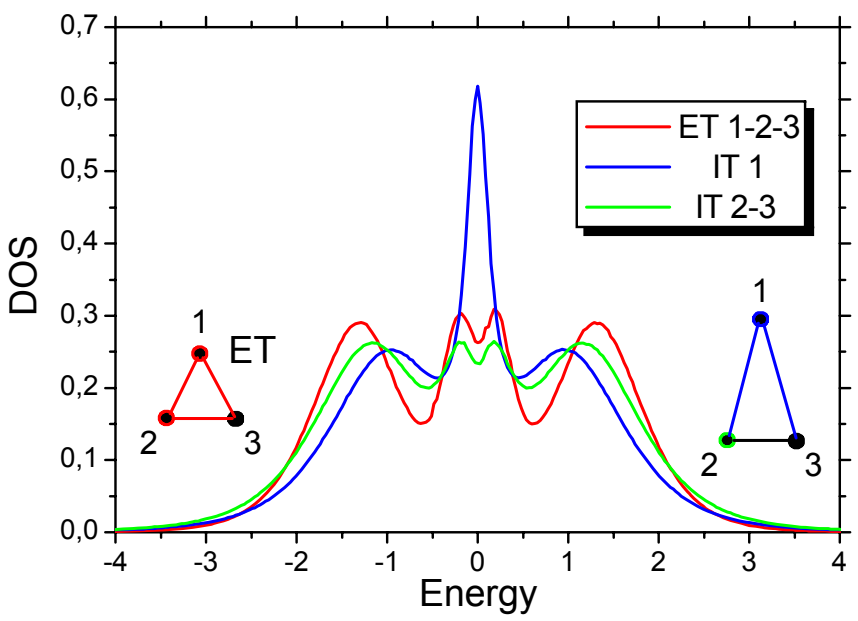
Equilateral and Isosceles Trimers

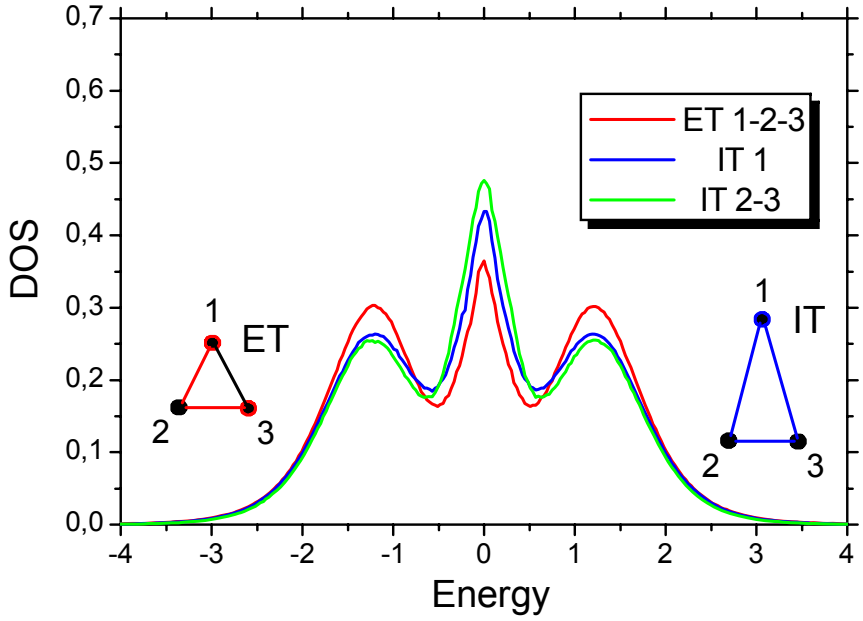
Density of states at geometry modification of the trimer

Equilateral (ET) and isosceles (IT) trimers

AFM $J_{23}=J,\ J_{12}=J_{13}=J/3$ **FM**

V. Savkin et al, PRL **94**, 026402 (2005)



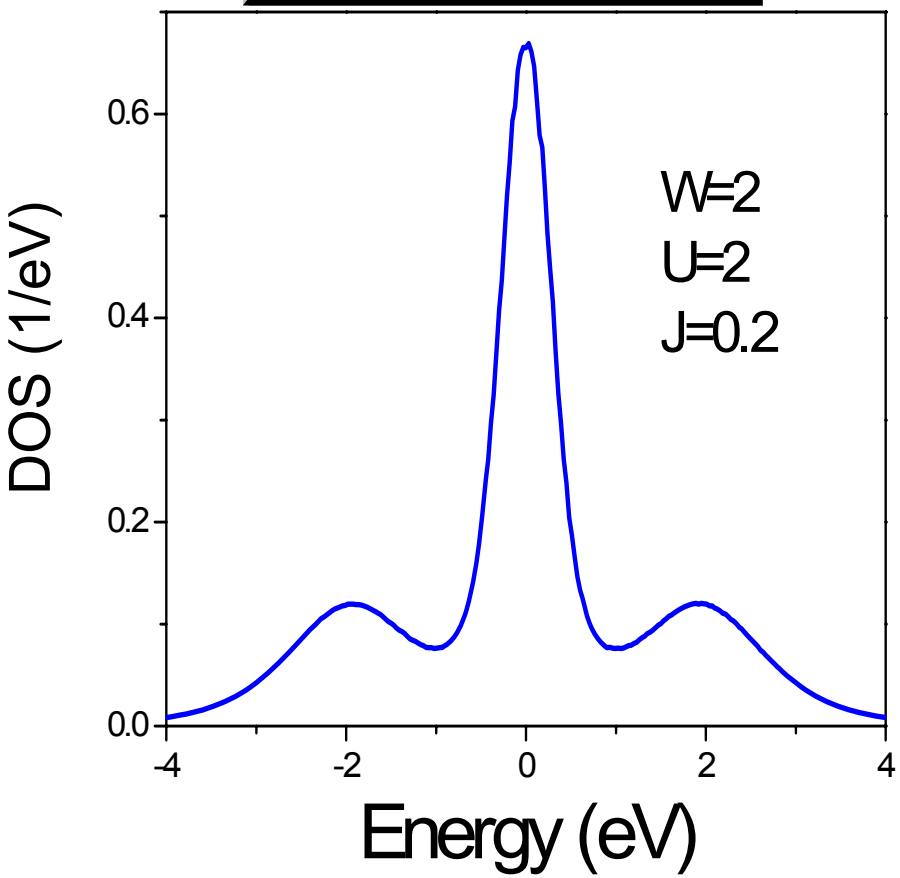


One can see a reconstruction of the Kondo resonance for isosceles trimer at antiferromagnetic exchange interaction

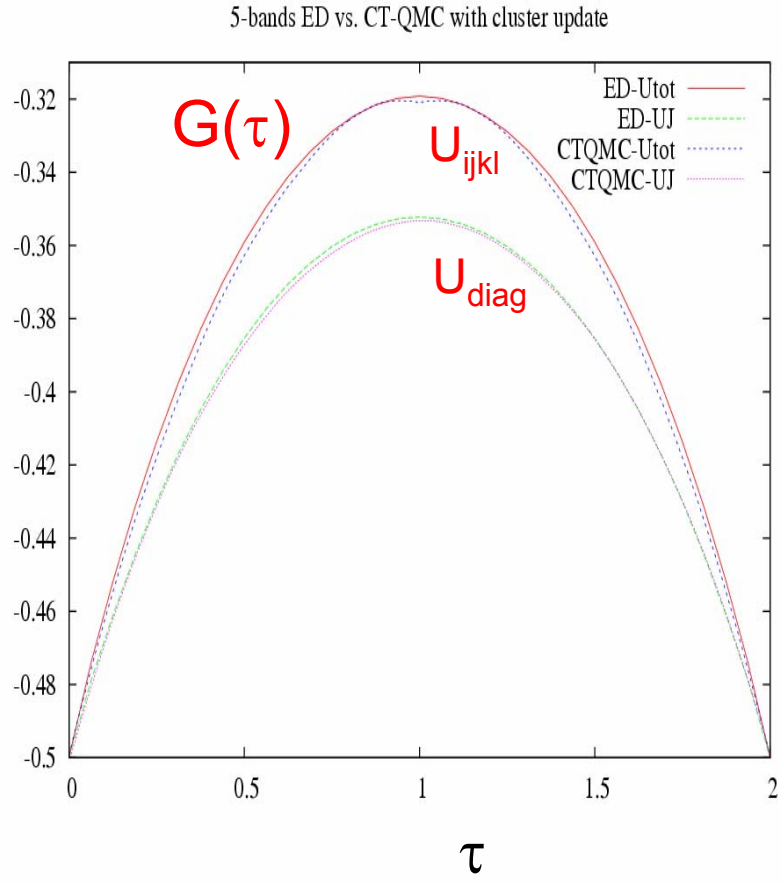
Multiorbital CT-QMC: general U-vertex

$$H = \sum_{ij\sigma} t_{ij} c^{+}_{i\sigma} c_{j\sigma} + \frac{1}{2} \sum_{ijkl\sigma\sigma'} U_{ijkl} c^{+}_{i\sigma} c^{+}_{i\sigma'} c_{l\sigma'} c_{k\sigma}$$

5 orbitals, full U-vertex

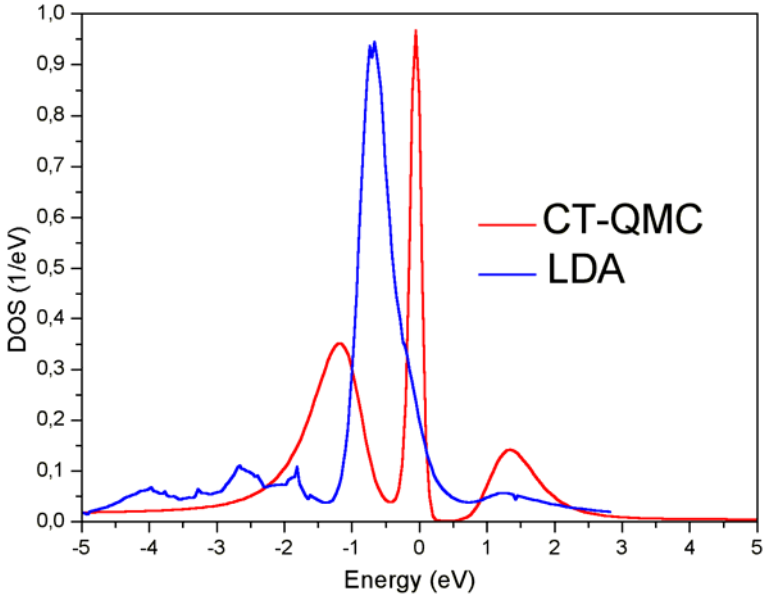


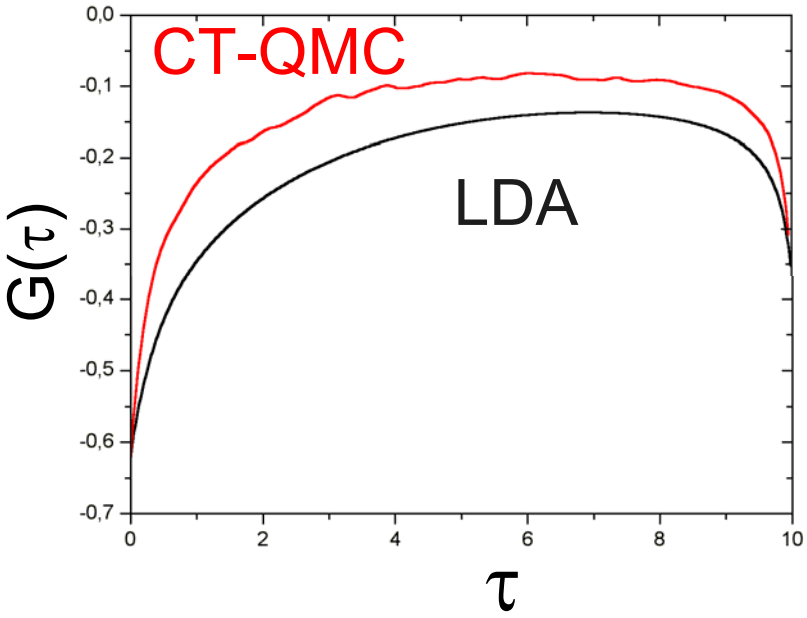
A. Rubtsov and A.L., JETP Lett. (2004)



E. Gorelov, et. al. to be published

Co in Cu 5d-orbitals QMC calculation



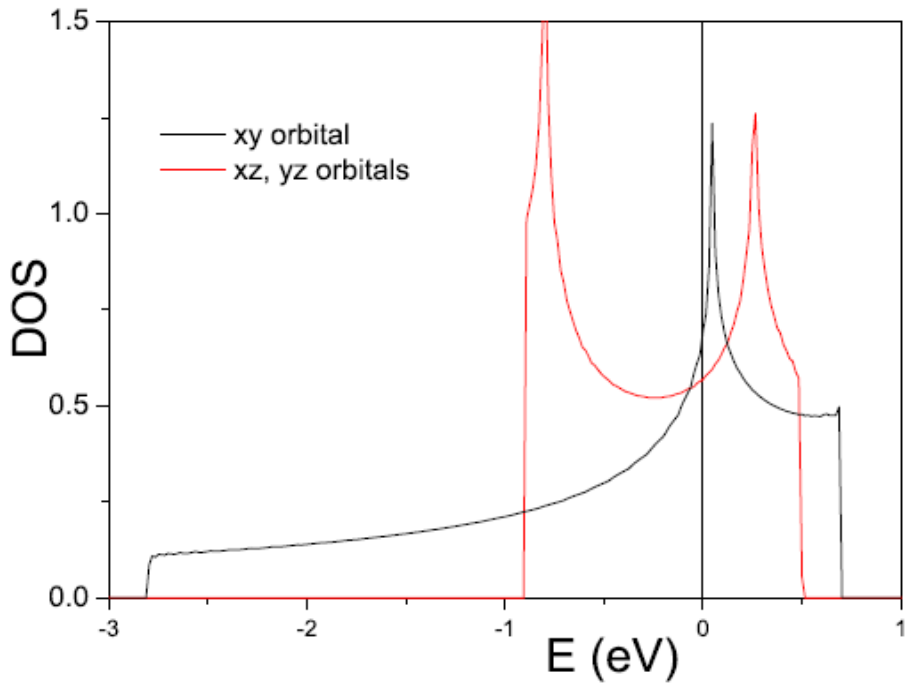


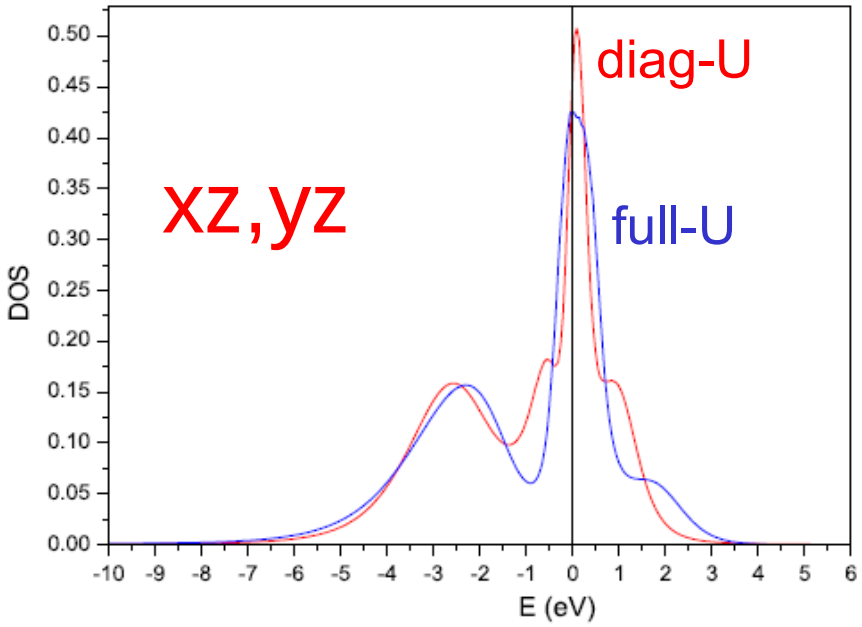
DOS for Co atom in Cu

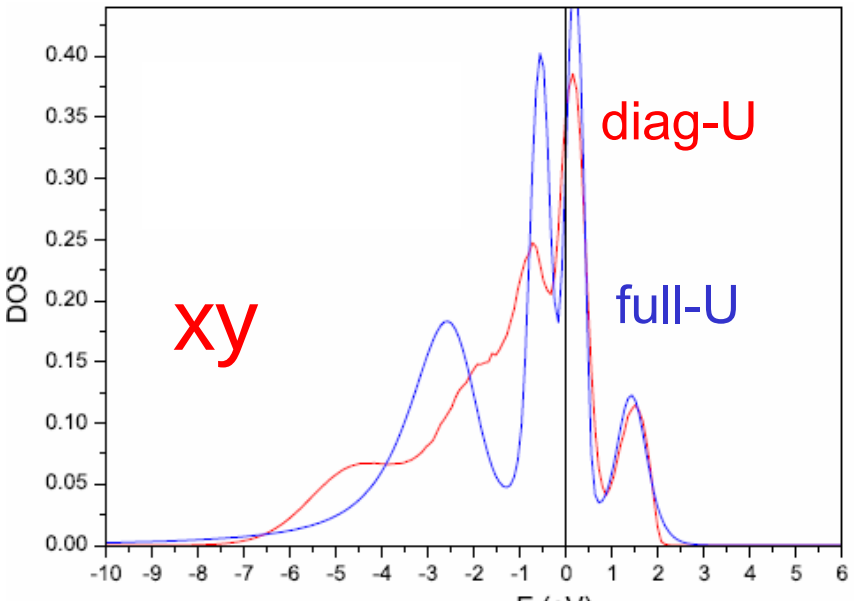
U=4, b = 10 (T ~ 1/40 W)

E. Gorelov et al, to be published

Effect of spin-flip on d^2: Sr_2RuO_4



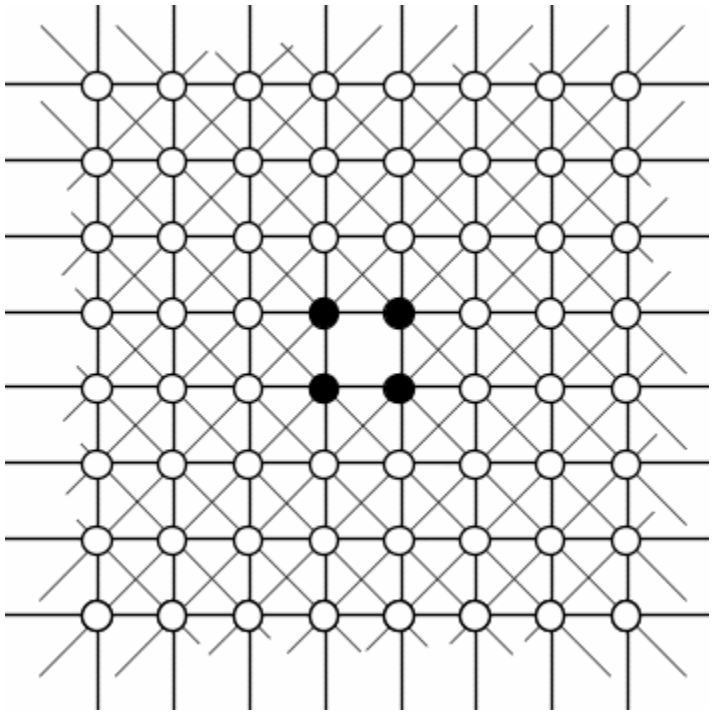




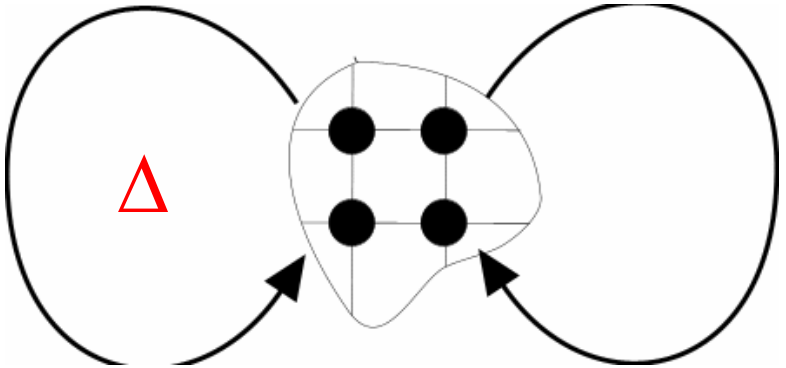
TB-model
A. Liebsch and A.L., PRL (2000)

DMFT with full-U, β=10

Beyond Cluster DMFT



short-range fluctuations



How to include exact k-dependence for correlated systems?

- Dynamical Vertex Approximation (K. Held, H. Kusunosa M. Jarrell)
- Dual Fermion Approximation (A. Rubtsov)

Beyond DMFT: Dual Fermion scheme

General Lattice Action $H = h + U$

$$S[c^*, c] = \sum_{\omega k m m' \sigma} \left[h_k^{mm'} - (i\omega + \mu) 1 \right] c^*_{\omega k m \sigma} c_{\omega k m' \sigma} + \frac{1}{4} \sum_{i\{m,\sigma\}} \int_0^\beta U_{1234} c_1^* c_2^* c_4 c_3 d\tau$$

Optimal Local Action with hybridization Δ_ω

$$S_{loc} = \sum_{\omega m m' \sigma} \left[\Delta_\omega^{mm'} - (i\omega + \mu) 1 \right] c^*_{\omega m \sigma} c_{\omega m' \sigma} + \frac{1}{4} \sum_{i\{m,\sigma\}} \int_0^\beta U_{1234} c_1^* c_2^* c_4 c_3 d\tau$$

Lattice-Impurity connection:

$$S[c^*, c] = \sum_i S_{loc}[c_i^*, c_i] + \sum_{\omega k m m' \sigma} \left(h_k^{mm'} - \Delta_\omega^{mm'} \right) c^*_{\omega k m \sigma} c_{\omega k m' \sigma}.$$

expand

A. Rubtsov, *et al* cond-mat/0612196

Dual Fermion transformation

Gaussian path-integral (Vector-Matrix notation)

$$\int D[\vec{f}^*, \vec{f}] \exp(-\vec{f}^* \hat{A} \vec{f} + \vec{f}^* \hat{B} \vec{c} + \vec{c}^* \hat{B} \vec{f}) = \det(\hat{A}) \exp(\vec{c}^* \hat{B} \hat{A}^{-1} \hat{B} \vec{c})$$

With $A = g_\omega^{-1}(\Delta_\omega - h_k) g_\omega^{-1}$, $B = g_\omega^{-1}$

new Action:

$$S_d[f^*, f] = -\sum_{k\omega\sigma} \mathcal{G}^{-1}_{k\omega\sigma} f^*_{k\omega\sigma} f_{k\omega\sigma} + \frac{1}{4} \sum_{1234} \gamma^{(4)}_{1234} f^*_1 f^*_2 f_4 f_3 + \gamma^{(6)} \ldots$$

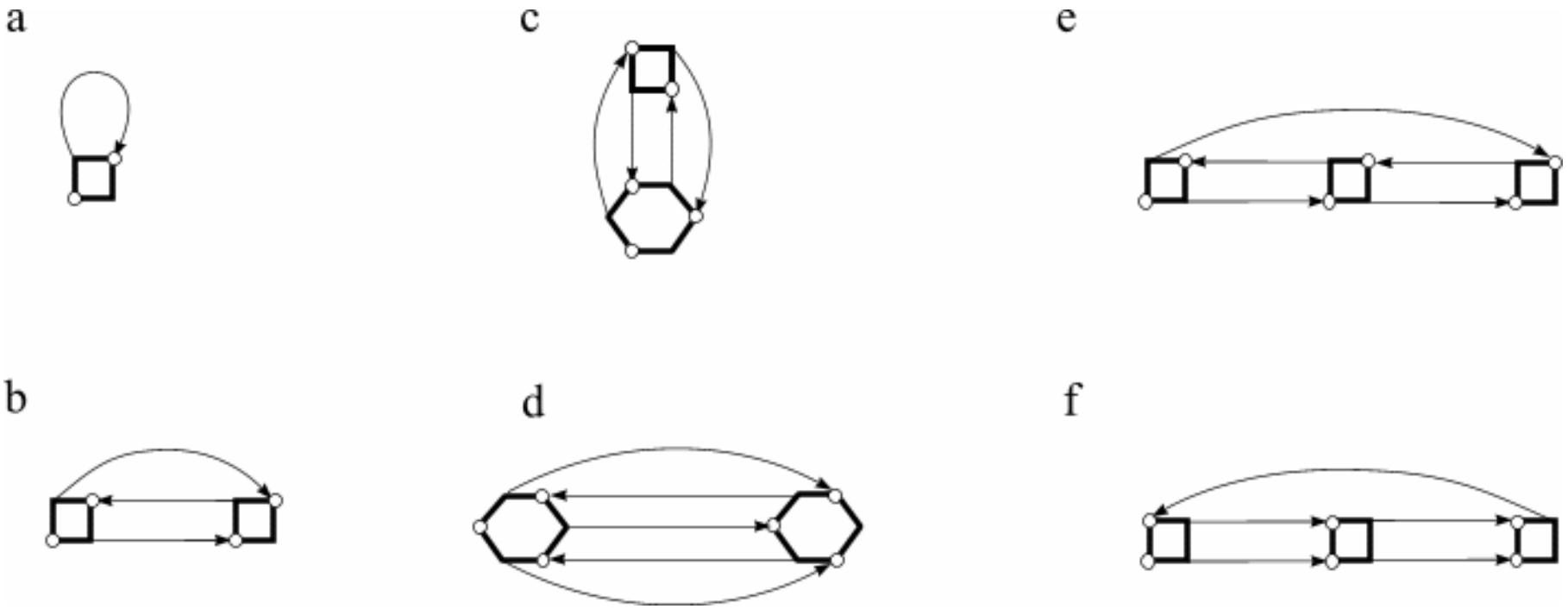
here:

$$\longrightarrow \quad \mathcal{G}^{-1}_{k\omega} = [g_\omega (h_k - \Delta_\omega) g_\omega]^{-1} - g_\omega^{-1}$$

$$\square \quad \gamma^{(4)}_{1234} = g^{-1}_{11'} g^{-1}_{22'} \left(\chi_{1'2'3'4'} - \chi^0_{1'2'3'4'}\right) g^{-1}_{3'3} g^{-1}_{4'4}$$

g_ω and $\chi_{\nu,\nu',\omega}$ from cDMFT

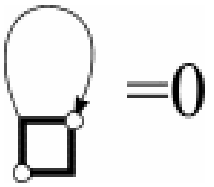
Basic diagrams for dual self-energy



Lines denote the renormalized Green's function.

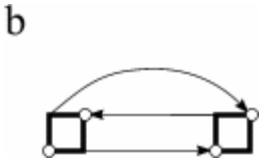
Condition for Δ and relation with DMFT

To determine Δ, we require
that Hartree correction in dual variables vanishes.
If no higher diagrams are taken into account, one obtains DMFT:



$$\sum_k \mathcal{G}^d_{k\omega} = 0 \longrightarrow \sum_k \left[g_\omega - (h_k - \Delta_\omega)^{-1} \right]^{-1} = 0$$

Higher-order diagrams give corrections to the DMFT self-energy,
and already the leading-order correction is nonlocal.



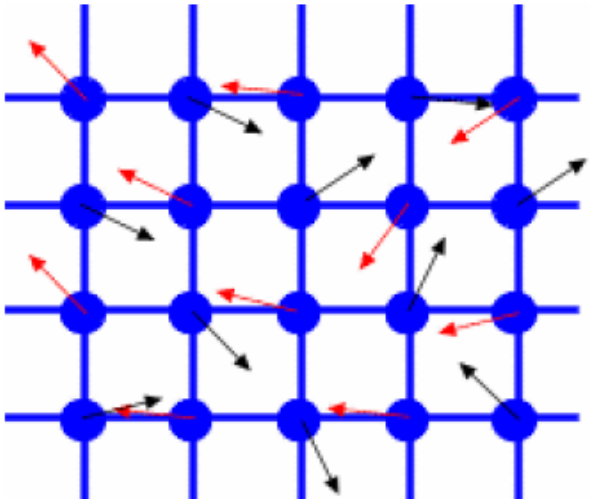
$\Sigma(k,\omega)$

Pseudogap in HTSC: dual fermions

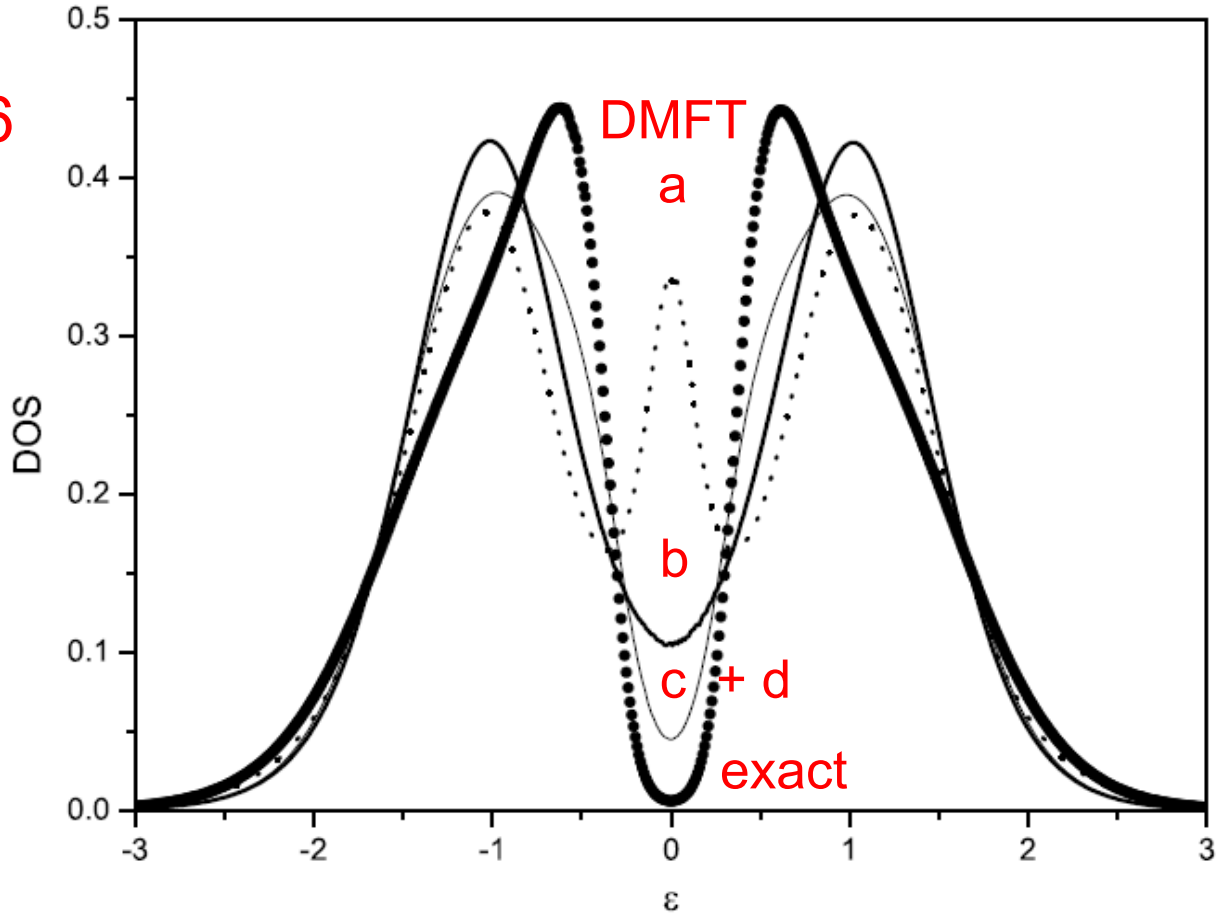
$$S[f,f^*] = \sum_{\omega k \sigma} g_\omega^{-2} \left((\Delta_\omega - \epsilon_k)^{-1} + g_\omega \right) f^*_{\omega k \sigma} f_{\omega k \sigma} + \sum_i V_i$$

A. Rubtsov et al

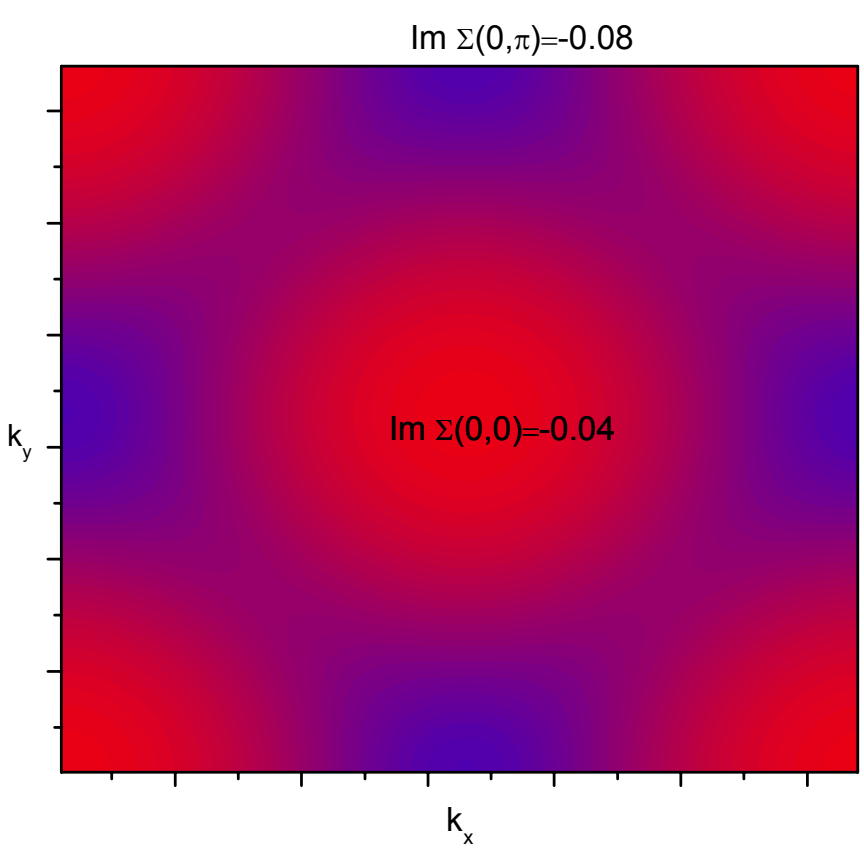
cond-mat/0612196

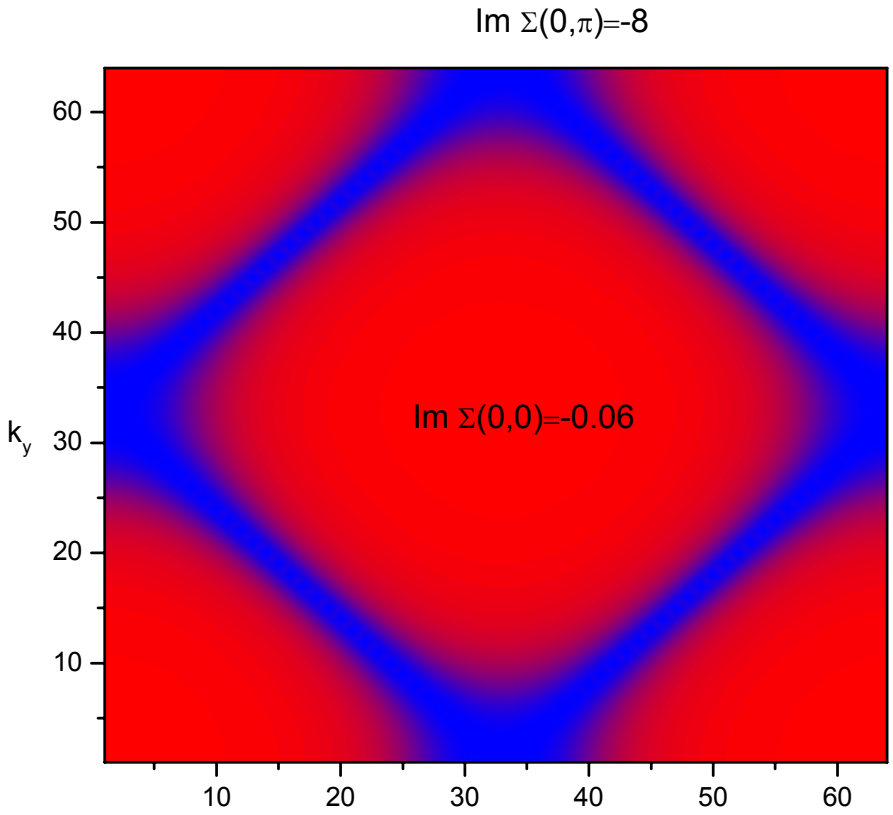


2d: U=W=2



2d-Hubbard ARPES: Im $\Sigma(k, \omega=0)$





U=1

W=2, β=20

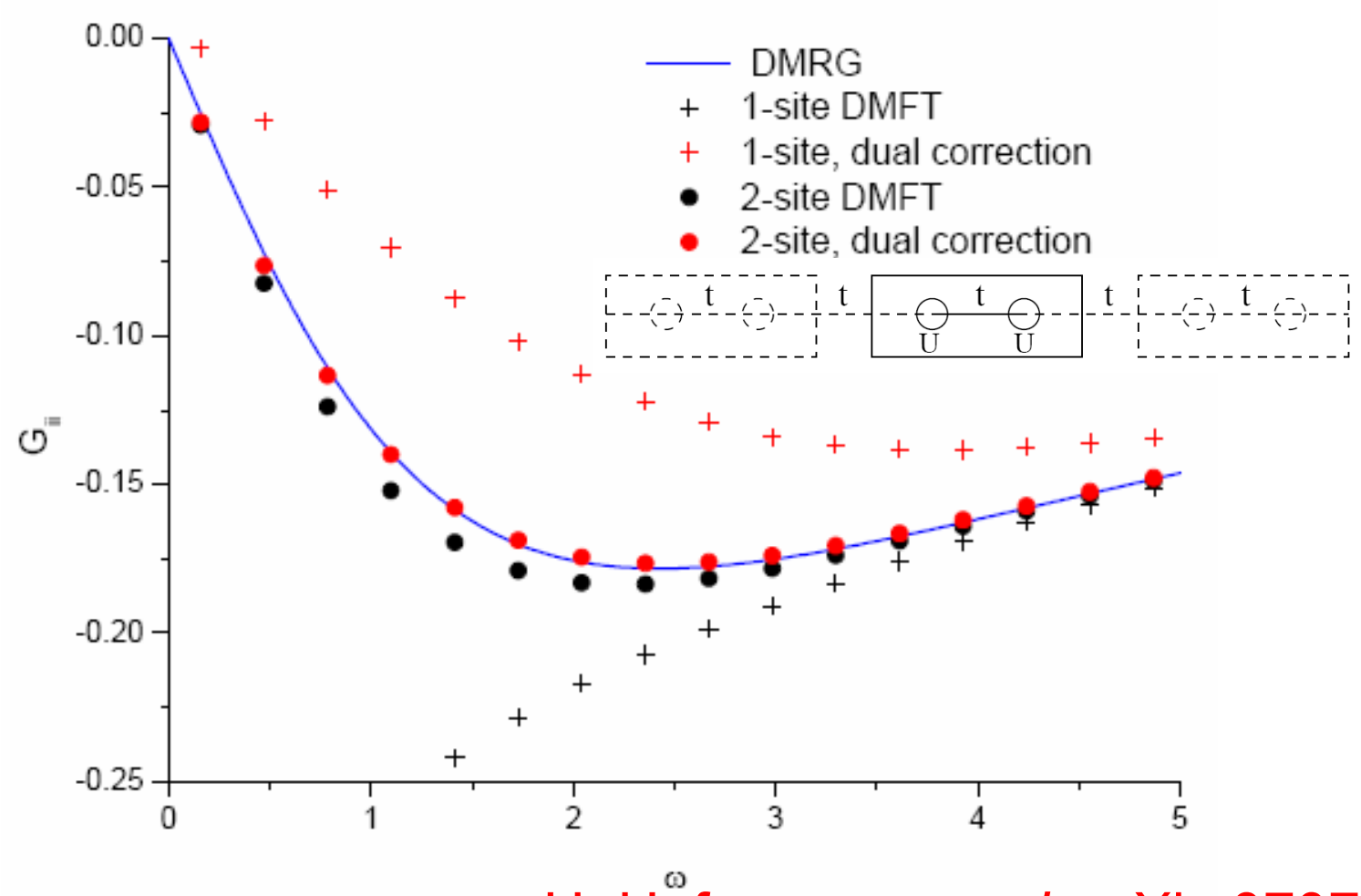
U=2

Near Mott transition self-energy is strongly k-dependent

In real materials – spin and orbital fluctuations!

Cluster Dual Fermions: 1d-test, n=1

1D Hubbard chain $U/t = 6$, $\beta = 10$, $\epsilon(\mathbf{k}) = -2t\cos(ka)$



H. Hafermann, *et al.* arXiv:0707.4022

Conclusions and perspectives

- LDA+DMFT is a simplest scheme for realistic description of electronic structure and magnetism of correlation electron materials
- Cluster LDA+DMFT method can be useful for the short-range non-local spin and orbital fluctuations in solids near Mott transition
- Multi-orbital DMFT calculation with general interaction vertex is possible in CT-QMC scheme
- Spin and Orbital in real materials near MIT can be investigated with k-dependent Dual Fermion approach