

Orbital-selective behavior in dimerized systems



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Motivation: suppression of the magnetic moments in dimers of 4d/5d metals

	Elec. conf.	Theoretical	Experimental
$\text{Y}_5\text{Mo}_2\text{O}_{12}$	$4d^{1.5}$	$\mu_{eff} = 3.24\mu_B/\text{dimer}$	$\mu_{eff} = 1.7\mu_B/\text{dimer}$
$\text{Ba}_5\text{YRu}_2\text{O}_9$	$4d^{3.5}$	$\mu = 2\mu_B/\text{Ru}$	$\mu = 0.56\mu_B/\text{Ru}$
$\text{Ba}_5\text{AlIr}_2\text{O}_{11}$	$5d^{4.5}$	$\mu_{eff} = 3.32\mu_B/\text{dimer}$	$\mu_{eff} \sim 1.04\mu_B/\text{dimer}$
$\text{Ba}_5\text{NaOs}_2\text{O}_9$	$4d^{3.5}$	$\mu_{eff} = 4.78\mu_B/\text{Os}$	$\mu_{eff} = 3.34\mu_B/\text{Os}$

etc.

How to explain?

1. Hybridization effects
2. Spin-orbit coupling



Common wisdom

3. Orbital-selective behaviour!

Outline:

- 1. Introduction;**
- 2. Orbital-selective behaviour – model treatment;**
- 3. Orbital-selective behaviour –
examples of the real systems;**
- 4. Double exchange vs. molecular orbitals;**
- 5. Role of the spin-orbit coupling (example).**

Introduction (theoretical): Dimer

(1 orbital, 1 electron per site)



e.g. H₂

Molecular-orbital:

$$|MO\rangle = \frac{1}{2} |(c_{1\uparrow}^\dagger + c_{2\uparrow}^\dagger)(c_{1\downarrow}^\dagger + c_{2\downarrow}^\dagger)\rangle = \frac{1}{2} | \underbrace{c_{1\uparrow}^\dagger c_{1\downarrow}^\dagger}_{\uparrow\downarrow} - \underbrace{c_{1\uparrow}^\dagger c_{2\downarrow}^\dagger}_{\uparrow\downarrow} + \underbrace{c_{2\uparrow}^\dagger c_{1\downarrow}^\dagger}_{\downarrow\uparrow} - \underbrace{c_{2\uparrow}^\dagger c_{2\downarrow}^\dagger}_{\uparrow\downarrow} \rangle, \quad U/t \rightarrow 0$$

← “ionic” terms →

Heitler-London: $|HL\rangle = \frac{1}{\sqrt{2}} |c_{1\uparrow}^\dagger c_{2\downarrow}^\dagger - c_{1\downarrow}^\dagger c_{2\uparrow}^\dagger\rangle \quad U/t \rightarrow \infty$

Coulson-Fisher: $|CF\rangle = \frac{\cos \theta}{\sqrt{2}} | \underbrace{c_{1\uparrow}^\dagger c_{2\downarrow}^\dagger - c_{1\downarrow}^\dagger c_{2\uparrow}^\dagger}_{\text{“HL” terms}} \rangle + \frac{\sin \theta}{\sqrt{2}} | \underbrace{c_{1\uparrow}^\dagger c_{1\downarrow}^\dagger + c_{2\uparrow}^\dagger c_{2\downarrow}^\dagger}_{\text{“ionic” terms}} \rangle$

VO₂: $\frac{\text{Ionic terms}}{\text{HL terms}} = \frac{1}{8}$

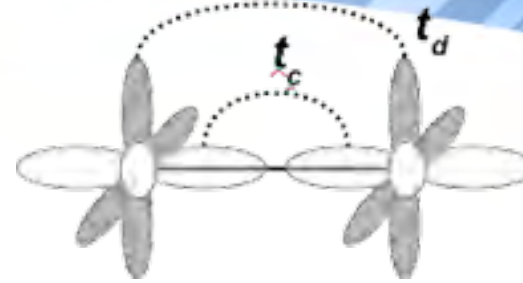
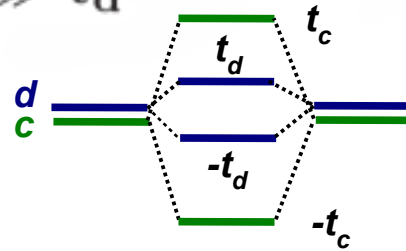
Belozarov et al. PRB 85, 045109 (2012)

Introduction (theoretical): Dimer

(few orbitals, few electrons per site)

- **Two** orbitals/site
- **Two** electrons/site (four/dimer)

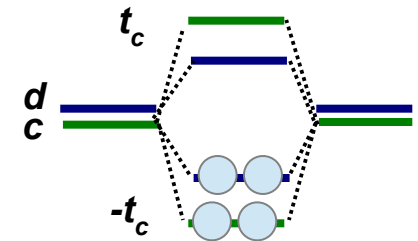
$$t_c \gg t_d$$



$$(t_c, t_d) \gg (U, J_H)$$

c, d – electrons: molecular orbital

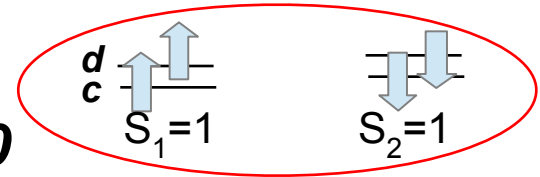
$$S=0$$



$$(U, J_H) \gg (t_c, t_d)$$

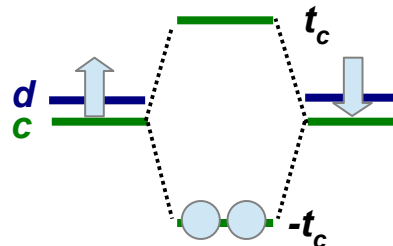
Heitler-London wave function

$$S=0$$



$$t_c \gg (J_H, U)$$

$$t_d \rightarrow 0$$



c – electrons: molecular orbit ($s_c=0$);

d – electrons: decoupled (may have local moments);

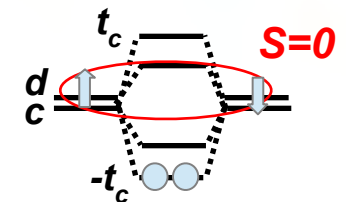
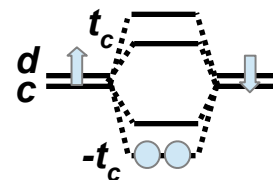
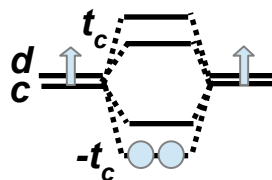
Orbital-selective behaviour!

Orbital-selective physics in dimers: choice of the wave-function

1) Molecular-orbit limit: $t_c \gg (J_H, U), t_c \gg t_d, n_i > 1$

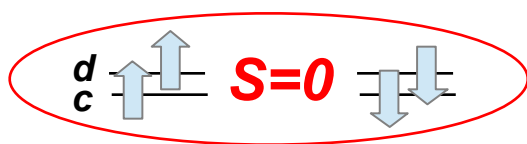
$$|\widetilde{MO}\rangle = \frac{1}{2}[(c_{1\uparrow}^\dagger + c_{2\uparrow}^\dagger)(c_{1\downarrow}^\dagger + c_{2\downarrow}^\dagger)\Psi_d],$$

OS regime!



$$\Psi_d^{FM} = |d_{1\uparrow}^\dagger d_{2\uparrow}^\dagger\rangle, \quad \Psi_d^{AFM} = |d_{1\uparrow}^\dagger d_{2\downarrow}^\dagger\rangle, \quad \Psi_d^{HL} = \frac{1}{\sqrt{2}}(|d_{1\uparrow}^\dagger d_{2\downarrow}^\dagger\rangle - |d_{1\downarrow}^\dagger d_{2\uparrow}^\dagger\rangle)$$

2) Heitler-London limit: $(J_H, U) \gg (t_d, t_c), t_d \neq t_c$



no OS behavior

$$|\widetilde{HL}\rangle = |S_{\text{tot}} = 0\rangle = \frac{1}{\sqrt{3}}(|S_1^z = 1, S_2^z = -1\rangle + |S_1^z = -1, S_2^z = 1\rangle - |S_1^z = 0, S_2^z = 0\rangle)$$

$$= \frac{1}{\sqrt{3}}(|c_{1\uparrow}^\dagger d_{1\uparrow}^\dagger c_{2\downarrow}^\dagger d_{2\downarrow}^\dagger\rangle + |c_{1\downarrow}^\dagger d_{1\downarrow}^\dagger c_{2\uparrow}^\dagger d_{2\uparrow}^\dagger\rangle - \frac{1}{2}(|c_{1\uparrow}^\dagger d_{1\downarrow}^\dagger + c_{1\downarrow}^\dagger d_{1\uparrow}^\dagger\rangle(|c_{2\uparrow}^\dagger d_{2\downarrow}^\dagger + c_{2\downarrow}^\dagger d_{2\uparrow}^\dagger\rangle))$$

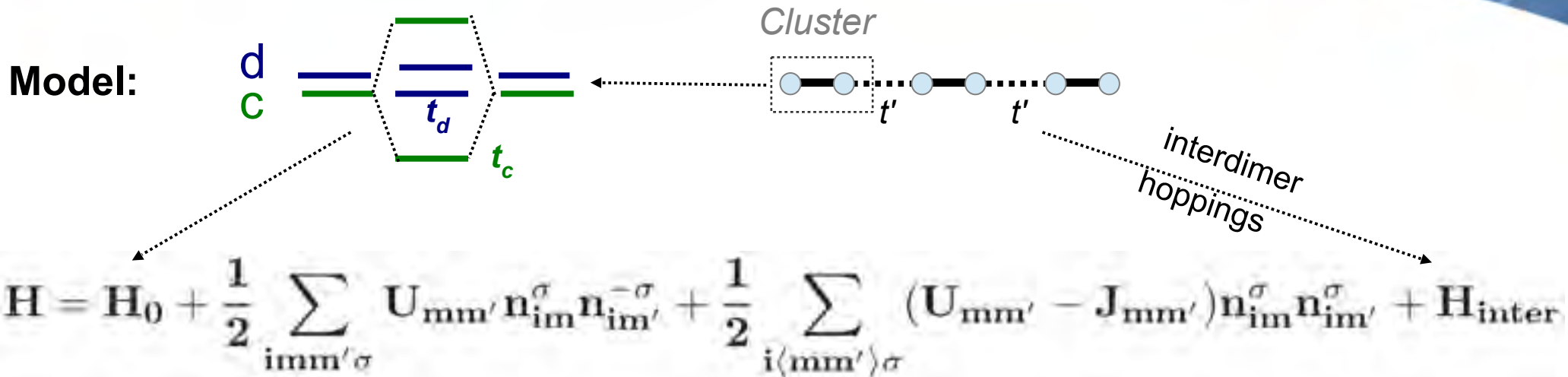
3) General treatment:

$$|\Psi\rangle = c(|\widetilde{MO}\rangle + \alpha|\widetilde{HL}\rangle)$$

c - normalization factor
 α - variational parameter

If $U \rightarrow 0$ then $\alpha \sim J_H/t_c$

Cluster-DMFT: calculation details

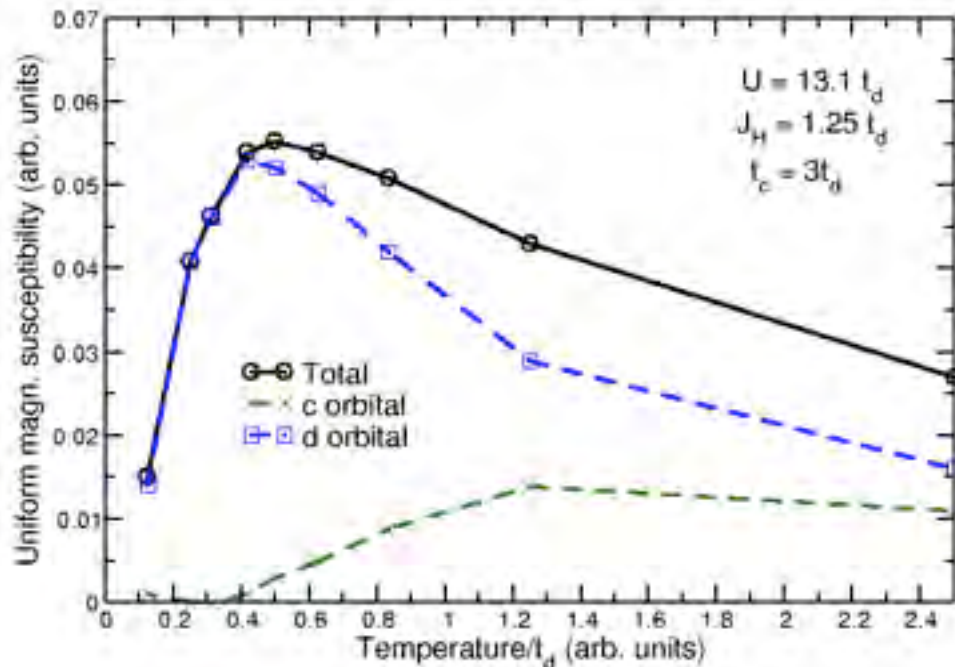


Solver: HF-QMC

$$\Sigma = \begin{pmatrix} \hat{\Sigma}^{11} & \hat{\Sigma}^{12} & 0 & 0 \\ \hat{\Sigma}^{21} & \hat{\Sigma}^{22} & 0 & 0 \\ 0 & 0 & \hat{\Sigma}^{11} & \hat{\Sigma}^{12} \\ 0 & 0 & \hat{\Sigma}^{21} & \hat{\Sigma}^{22} \end{pmatrix}$$

Uniform magnetic susceptibility: $\chi = M/B_{ext}$

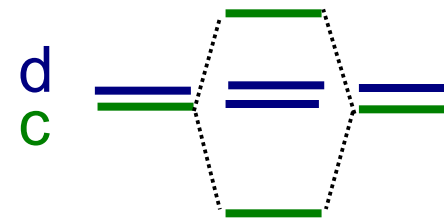
Cluster-DMFT: magnetic susceptibility



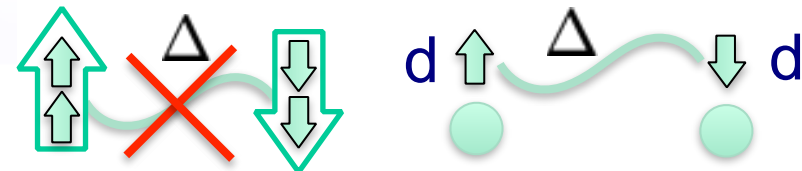
Orbital-selective behaviour!

Corollaries:

I. c and d orbitals “work” in different temperature regions!

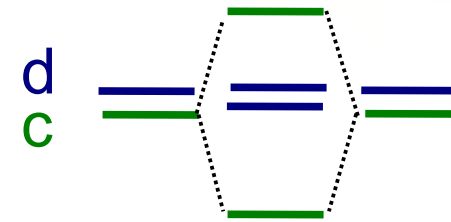
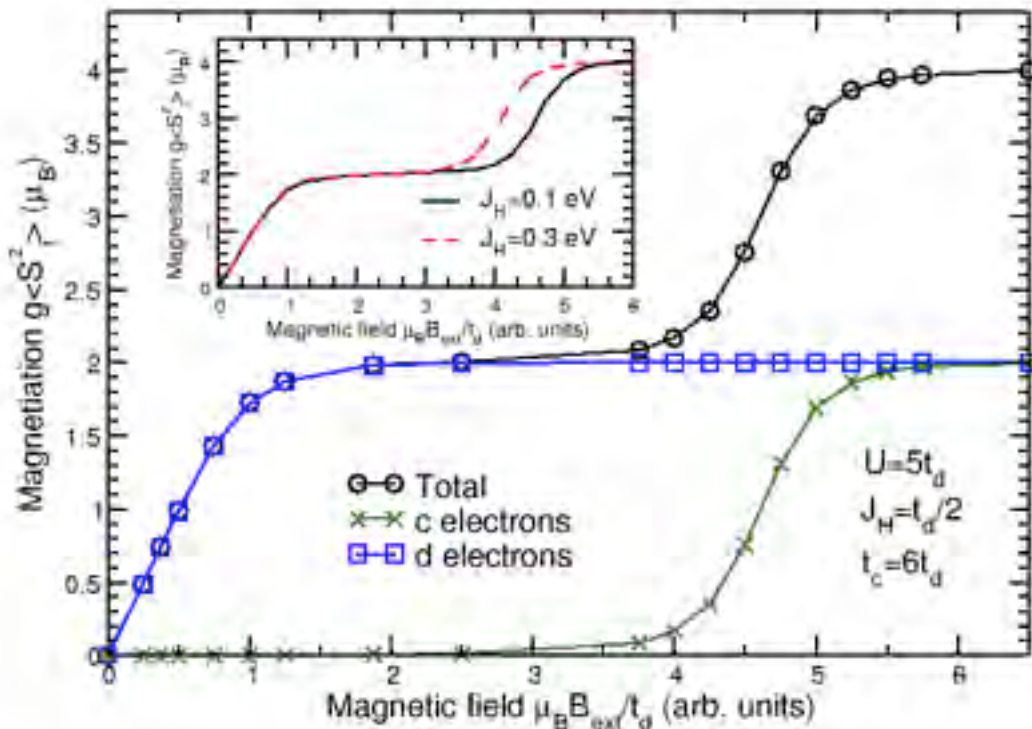


II. Be careful fitting experimental $\chi(T)$ with spins taken for isolated ions!



III. Dimer can be formed due to Peierls transition and then this will be orbital-selective Peierls transition

Cluster-DMFT: on-site spin moment in external magnetic field



1. Internal exchange field may play the same role as external one;
2. The “width” of the orbital-selective region depends on J_H/t_c

↑ Only d-electrons (localized) are magnetized ↑ c-electrons (MO) starts to magnetize ↑ Both electrons are magnetized

Orbital-selective regime

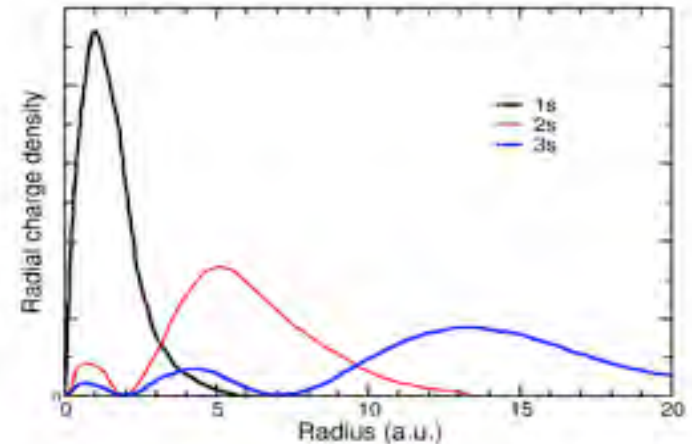
Orbital-selective behaviour: where to expect?

Requirements: $t_c \gg t_d$, $t_c > J_H$

$$3d \rightarrow 4d - 5d$$

Wave functions become more extended

t – increasing, J_H – decreasing



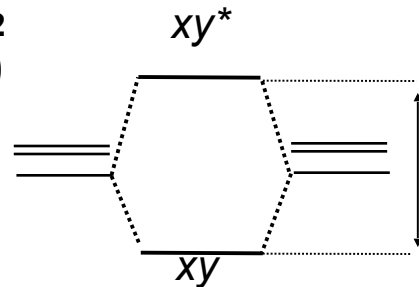
I.e. in the $4d$ - $5d$ transition metal compounds!

Hund's exchange: E.g. $3d^4$ (Mn^{3+}): $J_H \sim 0.9$ - 1 eV; $4d^4$ (Ru^{4+}): $J_H \sim 0.7$ eV

Hoppings:

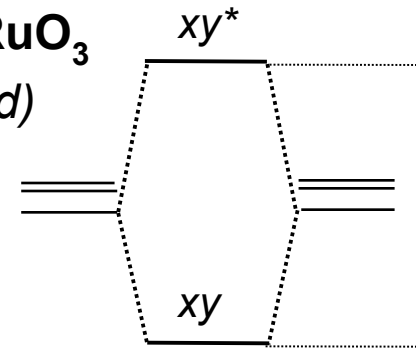
E.g. edge sharing octahedra

VO_2
($3d$)



$2t \sim 1.4$ eV

Li_2RuO_3
($4d$)



$2t \sim 2.2$ eV

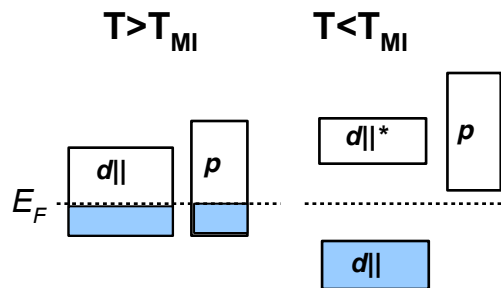
Example: MoO₂

VO₂ (3d¹)

Rutile structure; $T < T_{MI}$ dimerized chains of VO₆ sharing common edge

Metal-insulator transition at $T_{MI} = 340$ K

Spin singlet $T < T_{MI}$; Curie-Weiss PM $T > T_{MI}$



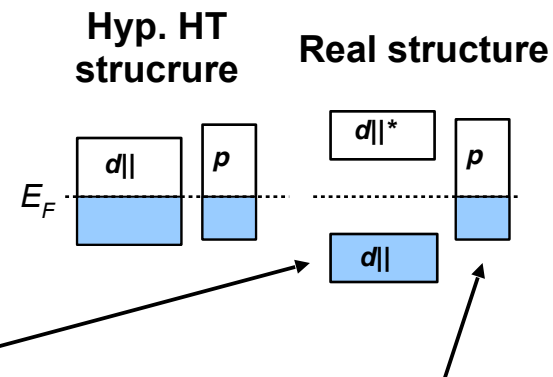
“c” electrons form molecular orbitals

MoO₂ (4d²)

Rutile structure; **Dimerized** chains of MoO₆ sharing common edge

Metal

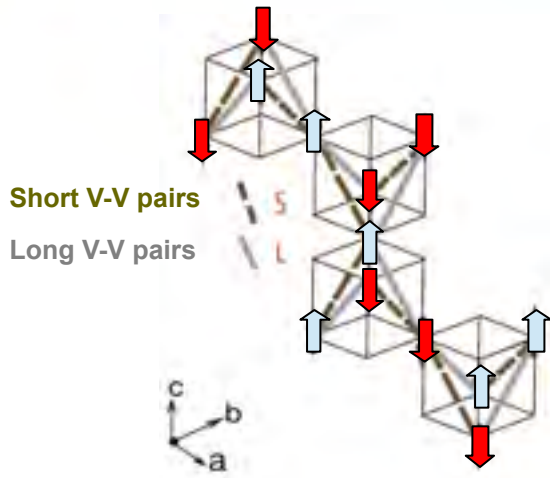
Pauli PM



“d” electrons provide metallic band

Example: CdV_2O_4 (V^{3+} , $3d^2$)

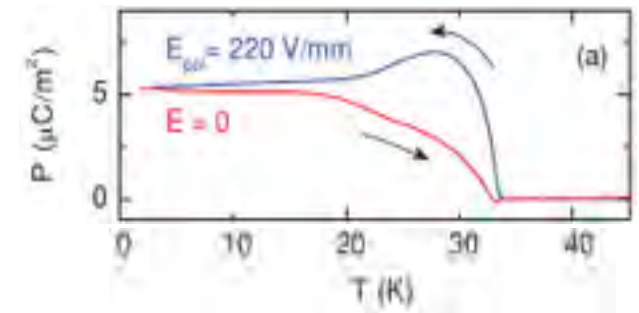
Experiment



Magnetic structure for $T < 33$ K:
chains $\uparrow\uparrow\downarrow\downarrow\uparrow\uparrow$
along $[101]$ and $[011]$

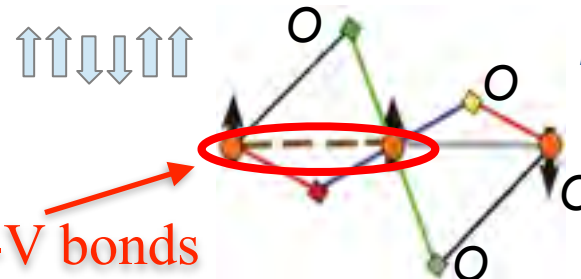
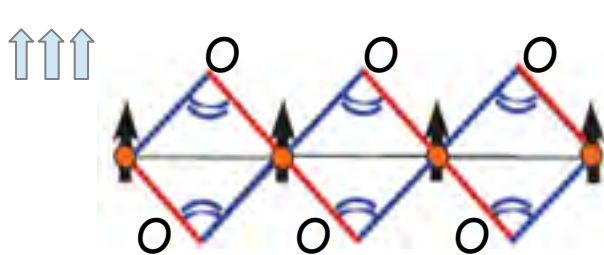
Insulator,
Multiferroic

M. Reehuis et al., Eur. Phys. J. B 35, 311 (2003)



GGA+U results:

Mechanism of the multiferroicity - magnetostriction



PRB 83, 060402(R) (2011)

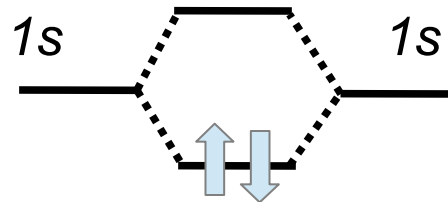
Why spins in $\text{V}^{3+}(d^2, S=1)$ dimers are FM ordered?

Why dimers in $(\text{Cd,Zn})\text{V}_2\text{O}_4$ are FM (triplet)?

Why spins in $\text{V}^{3+}(\text{d}^2, \text{S}=1)$ dimers are FM ordered?

$$\mu \sim 2\mu_B/V$$

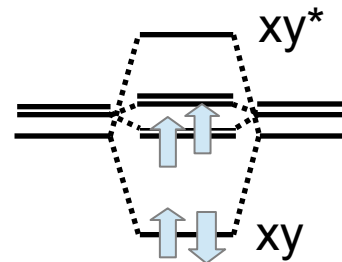
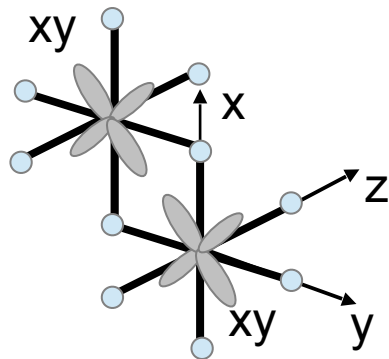
H_2 molecule



$\text{S}=0$ (AFM) !

Double exchange? No $(\text{Cd,Zn})\text{V}_2\text{O}_4$ - insulators

Strong overlap between xy orbitals in dimers



Orbital-selective physics
($\text{S}=1/2$ per V)

$$\mu \sim 1\mu_B/V$$

Indirect evidence:

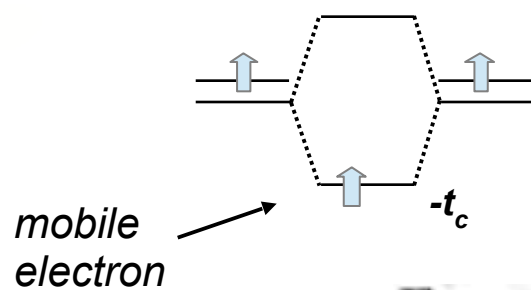
Magnetic mom.: $\mu = 0.65\mu_B/V$

Reehuis et al.,
EPJB 35, 311 (2003)

Molecular orbitals vs. double exchange

(orbital-selective behaviour for noninteger number of electrons)

Noninteger number of electrons (e.g. 1.5) per site!

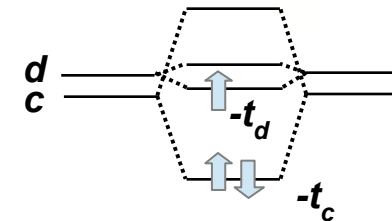


$$E_{DE} = -t_c - J_H$$

Double-exchange

$$S=3/2$$

3d transition metal oxides



$$E_{OS} = -2t_c - t_d - \frac{J_H}{2}$$

Orbital-selective regime

$$S=1/2$$

4d-5d transition metal oxides

Competition

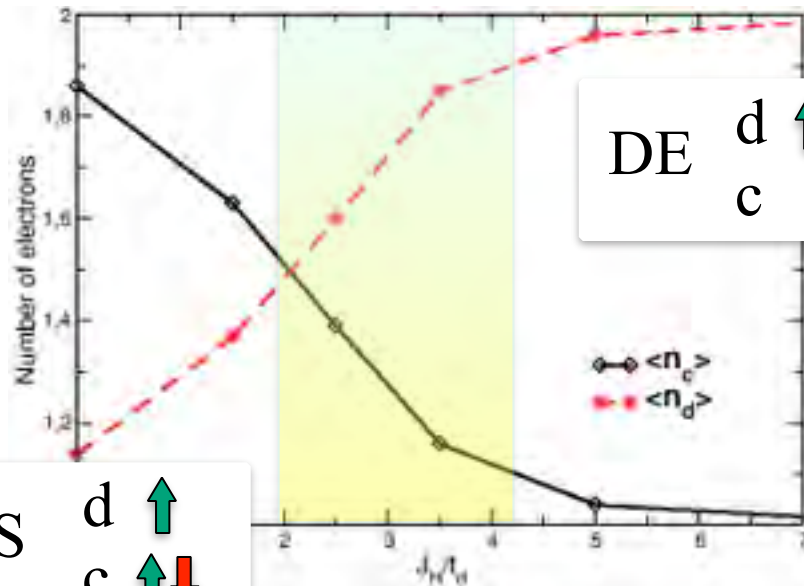
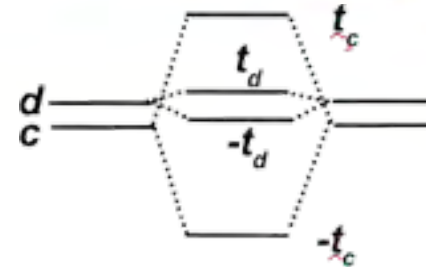
$$J_H \text{ vs. } 2(t_c + t_d)$$

Orbital-selective behaviour may suppress the double exchange mechanism of FM in the 4d and 5d transition metal oxides!

Suppression of the double exchange: model (DMFT) treatment

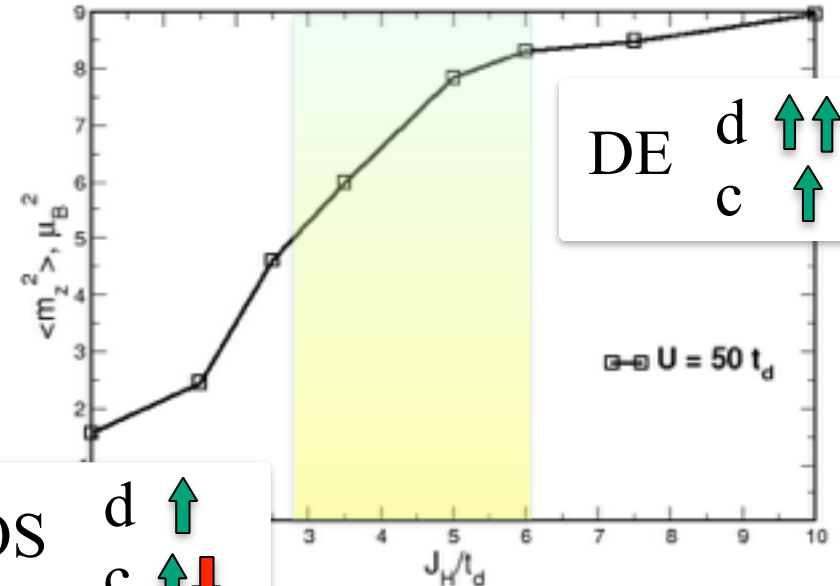
- Cluster DMFT
- HF-QMC, $T=0.1$ eV
- 2 bands; 1.5 electrons/site;
- $t_c=6t_d$, $U=50t_d$, $t'=0.5t_d$

Chain of dimers



DE d $\uparrow\uparrow$
c \uparrow

OS d \uparrow
c $\uparrow\downarrow$



DE d $\uparrow\uparrow$
c \uparrow

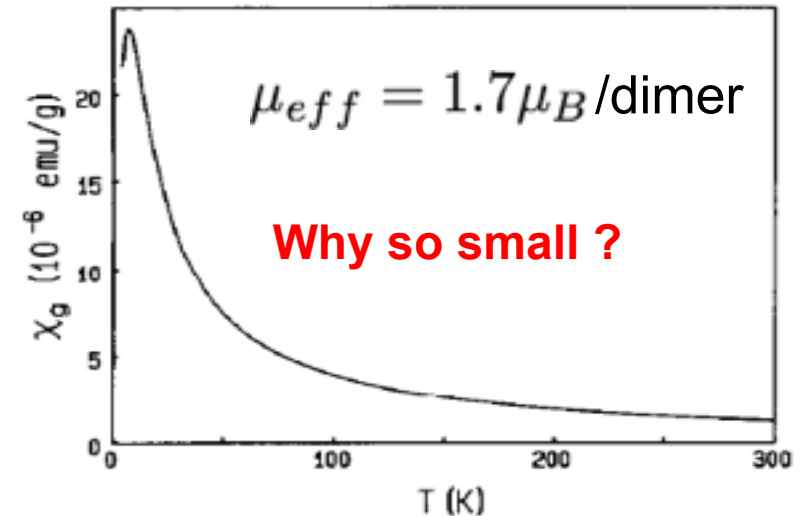
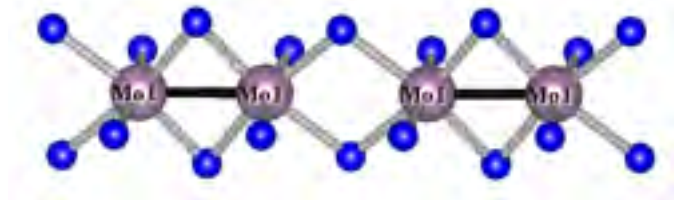
OS d \uparrow
c $\uparrow\downarrow$

There is crossover from the DE to OS

Example: $Y_5Mo_2O_{12}$

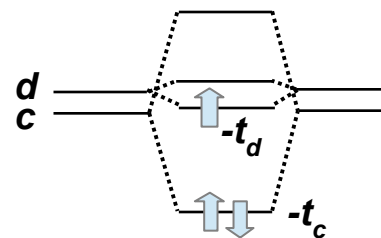
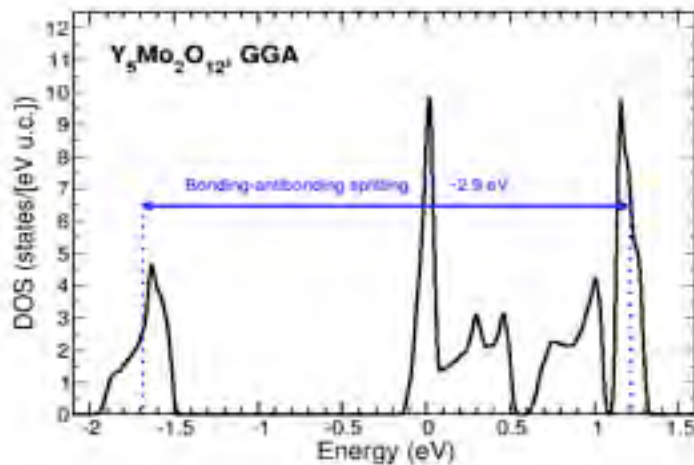
$Mo^{4.5+}: 4d^{1.5}$ $\mu_{eff} = 3.24\mu_B/\text{dimer}$

Crystal structure: dimerized chains



Torardi et al., *J. Solid State Chem* 60, 332 (1985)

GGA calculations:



$S=1/2$ per dimer

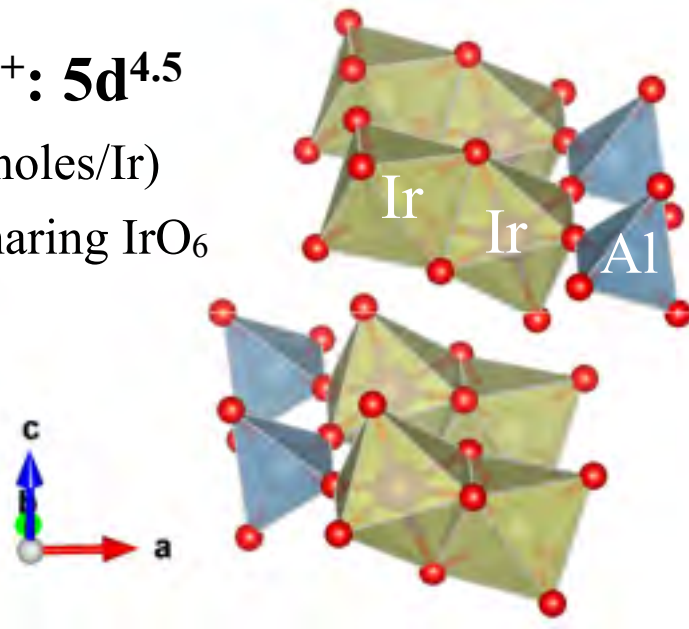
$\mu_{eff} = 1.73\mu_B/\text{dimer}$

Orbital-selective state is realized !

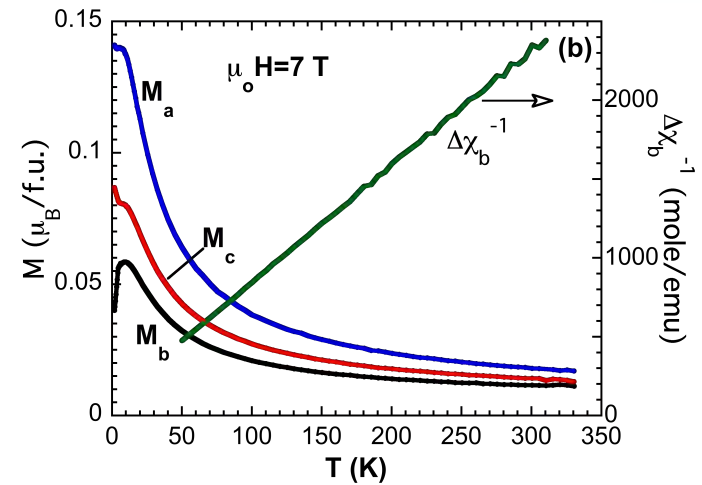
“c” electrons form MO
“d” retain local moments

More tricky example: $\text{Ba}_5\text{AlIr}_2\text{O}_{11}$

$\text{Ir}^{4.5+}: 5d^{4.5}$
(1.5 holes/Ir)
face-sharing IrO_6



Magnetic properties

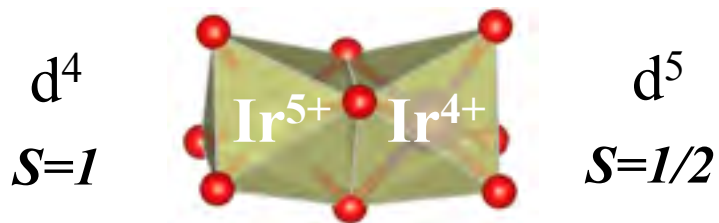


$$T_M = 4.5\text{K} \quad \theta_{CW} = -14\text{K}$$

$$\mu_{eff} \sim 1.04\mu_B/\text{dimer}$$

$T_{CO} = 210\text{ K}$ structural transition

VBS: charge ordering



Unusually small magnetic moment!

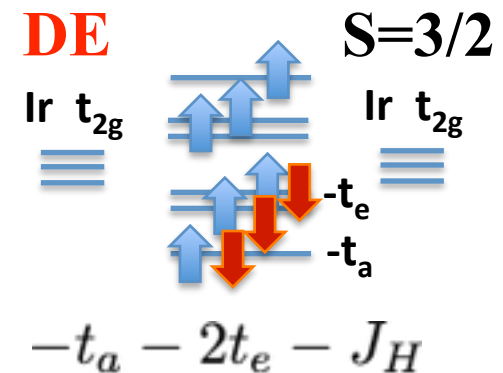
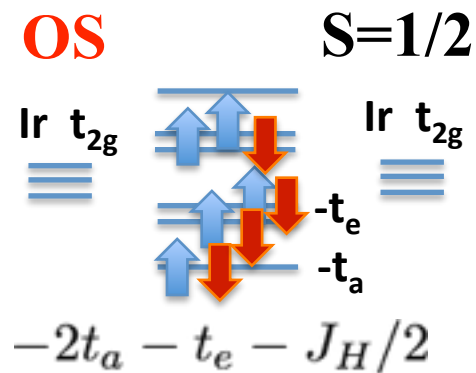
$J=0$ state doesn't explain small moment, since μ_{eff} is measured above T_{CO} .

More tricky example: $\text{Ba}_5\text{AlIr}_2\text{O}_{11}$ - GGA

GGA calculations

Moment: $\sim 2\mu_B/\text{dimer}$
 Type of order: Ferromagnetic

Ionic consideration



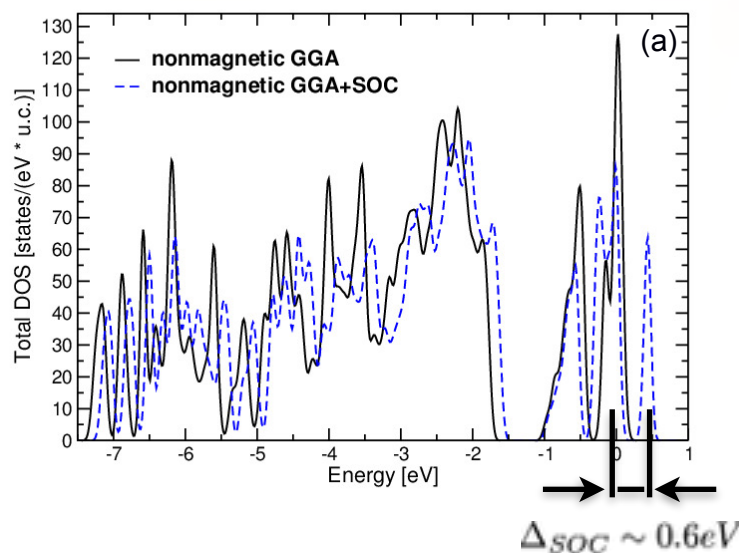
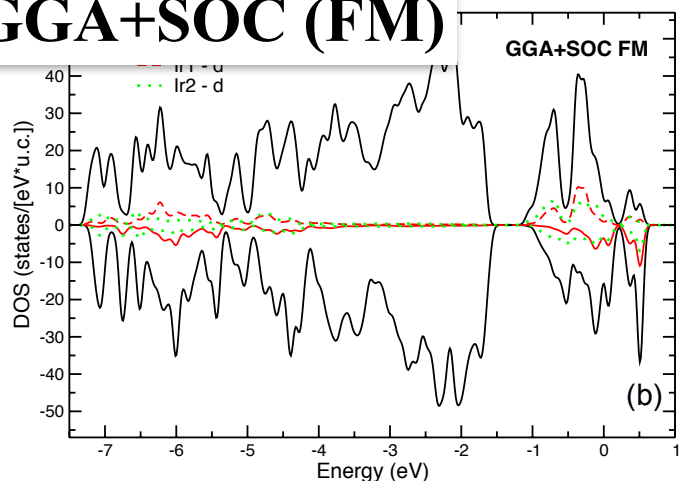
Therefore DE ($S=3/2$) state realizes if $J_H > 2(t_a - t_e)$

NM LDA $t_a - t_e \sim 0.2\text{eV}$
 $J_H \sim 0.5\text{eV}$

This is the reason why GGA gives solution with high moment

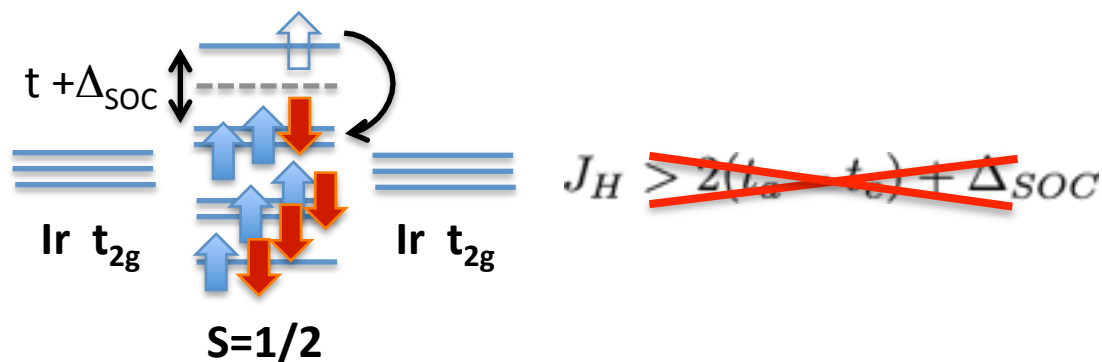
More tricky example: $\text{Ba}_5\text{AlIr}_2\text{O}_{11}$ - GGA+SOC

GGA+SOC (FM)



Total moment: $\sim 0.8\mu_B/\text{dimer}$

	spin mom.	orb mom.
Ir^{4+}	$0.53\mu_B$	$-0.09\mu_B$
Ir^{5+}	$0.24\mu_B$	$-0.11\mu_B$
interst.	$0.27\mu_B$	-

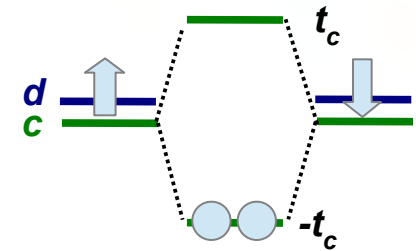


Moment decreases
not due to $J=0$ state of Ir^{5+}

The SOC conspires with strong covalency
(hopping) and helps to suppress DE

Summary

1. Electrons may be effectively decoupled and some of them may form spin-singlet state, while others provide FM, AFM or PM (orbital-selective behaviour);



2. This behaviour is more typical for $4d$ and $5d$ TM compounds (but not exclusively);

3. One may find many examples of such a behaviour (MoO_2 , CdV_2O_4 , $\text{Y}_5\text{Mo}_2\text{O}_{12}$, $\text{Y}_5\text{Re}_2\text{O}_{12}$, $\text{K}_2\text{Mo}_8\text{O}_{16}$ etc.)

4. Orbital-selective behaviour may suppress double exchange mechanism of FM $4d$ and $5d$ transition metal oxides;