Orbital-selective behavior in dimerized systems

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

<table>
<thead>
<tr>
<th>Elec. conf.</th>
<th>Theoretical</th>
<th>Experimental</th>
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<tr>
<td>Y$_5$Mo$<em>2$O$</em>{12}$</td>
<td>$\mu_{eff} = 3.24\mu_B$/dimer</td>
<td>$\mu_{eff} = 1.7\mu_B$/dimer</td>
</tr>
<tr>
<td>Ba$_5$YRu$_2$O$_9$</td>
<td>$\mu = 2\mu_B$/Ru</td>
<td>$\mu = 0.56\mu_B$/Ru</td>
</tr>
<tr>
<td>Ba$_5$AlIr$<em>2$O$</em>{11}$</td>
<td>$\mu_{eff} = 3.32\mu_B$/dimer</td>
<td>$\mu_{eff} \sim 1.04\mu_B$/dimer</td>
</tr>
<tr>
<td>Ba$_5$NaOs$_2$O$_9$</td>
<td>$\mu_{eff} = 4.78\mu_B$/Os</td>
<td>$\mu_{eff} = 3.34\mu_B$/Os</td>
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<tr>
<td>etc.</td>
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</table>

How to explain?  
1. Hybridization effects  
2. Spin-orbit coupling  
3. Orbital-selective behaviour!  

Common wisdom
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)

Molecular-orbital:

\[
|MO\rangle = \frac{1}{2} |(c_{1\uparrow} + c_{2\uparrow})(c_{1\downarrow} + c_{2\downarrow})\rangle = \frac{1}{2} |c_{1\uparrow} - c_{1\downarrow} + c_{2\uparrow} - c_{2\downarrow}\rangle, \quad U/t \rightarrow 0
\]

\text{e.g. } H_2

Heitler-London:

\[
|HL\rangle = \frac{1}{\sqrt{2}} |c_{1\uparrow} - c_{1\downarrow} c_{2\uparrow} - c_{2\downarrow}\rangle
\]

Coulson-Fisher:

\[
|CF\rangle = \frac{\cos \theta}{\sqrt{2}} |c_{1\uparrow} - c_{1\downarrow} c_{2\uparrow} + c_{2\downarrow}\rangle + \frac{\sin \theta}{\sqrt{2}} |c_{1\uparrow} + c_{2\uparrow} c_{2\downarrow}\rangle
\]

\[
\text{VO}_2: \quad \frac{\text{Ionic terms}}{\text{HL terms}} = \frac{1}{8}
\]

\text{Belozerov et al. PRB 85, 045109 (2012)}
**Introduction (theoretical): Dimer**
(few orbitals, few electrons per site)

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

\[(t_c, t_d) \gg (U, J_H)\]

\[(U, J_H) \gg (t_c, t_d)\]

\[t_c \gg (J_H, U)\]
\[t_d \to 0\]

**Heitler-London wave function**

\[S=0\]

\[c, d – \text{electrons: molecular orbital}\]

\[S=0\]

\[c – \text{electrons: molecular orbit (} s_c = 0);\]

\[d – \text{electrons: decoupled (may have local moments)};\]

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

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

\[
|\tilde{\text{MO}}\rangle = \frac{1}{2} |(c_{1\uparrow}^\dagger + c_{2\uparrow}^\dagger)(c_{1\downarrow}^\dagger + c_{2\downarrow}^\dagger)\rangle \Psi_d, \quad \text{OS regime!}
\]

\[
\Psi_d^{\text{FM}} = |d_{1\uparrow}^\dagger d_{2\uparrow}^\dagger\rangle, \quad \Psi_d^{\text{AFM}} = |d_{1\downarrow}^\dagger d_{2\downarrow}^\dagger\rangle, \quad \Psi_d^{\text{HL}} = \frac{1}{\sqrt{2}} |d_{1\uparrow}^\dagger d_{2\downarrow}^\dagger - d_{1\downarrow}^\dagger d_{2\uparrow}^\dagger\rangle
\]

2) Heitler-London limit:

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

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

no OS behavior

3) General treatment:

\[
|\Psi\rangle = c(|\tilde{\text{MO}}\rangle + \alpha|\tilde{\text{HL}}\rangle)
\]

If \( U \to 0 \) then \( \alpha \sim J_H / t_c \)

\( c \) - normalization factor
\( \alpha \) - variational parameter
Cluster-DMFT: calculation details

Model:

\[ H = H_0 + \frac{1}{2} \sum_{m, m', \sigma} U_{mm'} n_{im}^\sigma n_{im'}^{\sigma -} + \frac{1}{2} \sum_{i, (m, m')} (U_{mm'} - J_{mm'}) n_{im}^\sigma n_{im'}^\sigma + H_{\text{inter}} \]

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:

\[ \chi = M/B_{\text{ext}} \]
Cluster-DMFT: magnetic susceptibility

Corollaries:

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

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

Orbital-selective behaviour!

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 $J_H/t_c$

Orbital-selective regime
Orbital-selective behaviour: where to expect?

Requirements: \( t_c \gg t_d, \quad t_c > J_H \)

\[ 3d \rightarrow 4d - 5d \]

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

\( \text{VO}_2 \) (3d) \[ xy^* \]

\( \text{Li}_2\text{RuO}_3 \) (4d) \[ xy^* \]

2\( t \sim 1.4\) eV 2\( t \sim 2.2\) eV
Example: MoO$_2$

**VO$_2$ (3d$^1$)**

Rutile structure; $T<T_{\text{MI}}$ dimerized chains of VO$_6$ sharing common edge

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

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

**MoO$_2$ (4d$^2$)**

Rutile structure; Dimerized chains of MoO$_6$ sharing common edge

Metal

Pauli PM

---

“c” electrons form molecular orbitals

“d” electrons provide metallic band
Example: CdV$_2$O$_4$ (V$^{3+}$, 3d$^2$)

**Magnetic structure for T<33 K:**
- chains along [101] and [011]
- Insulator, Multiferroic


**GGA+U results:**
- Mechanism of the multiferroicity - magnetostriction

*PRB 83, 060402(R) (2011)*

Why spins in V$^{3+}$(d$^2$, S=1) dimers are FM ordered?
Why dimers in (Cd,Zn)V$_2$O$_4$ are FM (triplet)?

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

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

H$_2$ molecule

\[ \begin{array}{c}
1s \\
\hline
1s \\
\end{array} \]

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

Strong overlap between xy orbitals in dimers

Orbital-selective physics (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
(orital-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

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

Orbital-selective regime

S=3/2

3d transition metal oxides

S=1/2

4d-5d transition metal oxides

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

S.S. and D. Khomskii, PRB 89, 161112(R) (2014)
Suppression of the double exchange: model (DMFT) treatment

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

There is crossover from the DE to OS
Example: $Y_5Mo_2O_{12}$

$Mo^{4.5+}$: $4d^{1.5}$

$\mu_{eff} = 3.24\mu_B$/dimer

Crystal structure: dimerized chains

GGA calculations:

$\mu_{eff} = 1.7\mu_B$/dimer

Why so small?


Orbital-selective state is realized!

$S=1/2$ per dimer

"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 $\text{IrO}_6$

$\text{Ir}^{5+} \quad \text{Ir}^{4+}$
$\text{S}=1 \quad \text{S}=1/2$

$\text{T}_{\text{CO}} = 210 \text{ K structural transition}$

VBS: charge ordering

Magnetic properties

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

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

Unusually small magnetic moment!

$J=0$ state doesn’t explain small moment, since $\mu_{\text{eff}}$ is measured above $\text{T}_{\text{CO}}$. 
More tricky example: Ba$_5$AlIr$_2$O$_{11}$ - GGA

GGA calculations

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

Ionic consideration

OS S=1/2

DE S=3/2

$-2t_a - t_e - J_H/2$

$-t_a - 2t_e - J_H$

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

NM LDA

$t_a - t_e \sim 0.2eV$

$J_H \sim 0.5eV$

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: $\sim 0.8\mu_B$/dimer

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<thead>
<tr>
<th></th>
<th>spin mom.</th>
<th>orb mom.</th>
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<tbody>
<tr>
<td>$\text{Ir}^{4+}$</td>
<td>$0.53\mu_B$</td>
<td>$-0.09\mu_B$</td>
</tr>
<tr>
<td>$\text{Ir}^{5+}$</td>
<td>$0.24\mu_B$</td>
<td>$-0.11\mu_B$</td>
</tr>
<tr>
<td>interst.</td>
<td>$0.27\mu_B$</td>
<td>-</td>
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Moment decreases not due to $J=0$ state of $\text{Ir}^{5+}$

The SOC conspires with strong covalency (hopping) and helps to suppress DE
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$_2$O$_4$, Y$_5$Mo$_2$O$_{12}$, Y$_5$Re$_2$O$_{12}$, K$_2$Mo$_8$O$_{16}$ etc.)

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