Molecular orbitals vs. relativistic orbitals in t_{2g} honeycomb lattices: $SrRu_2O_6$ as compared to Na_2IrO_3, $RuCl_3$, and Li_2RuO_3.

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1. Hierarchy of one-electron energies: t, $\Delta=10Dq$, λ
2. Concept of quasi-molecular orbitals (QMO)
3. One hole (Kramers singlet) vs. two holes vs. three holes (half-filling).
4. Mysterious properties of $SrRu_2O_6$ and how they are explained through molecular orbitals

Na_2IrO_3: IIM, K. Foyevtseva, H. Jeschke, R. Valenti; $RuCl_3$: IIM, Y. Li, HJ, RV
Li_2RuO_3: IIM, S. Streltsov, J. Shen, D. Khomskii; $SrRu_2O_6$: IIM, SS, Z. Pchelkina

The importance of being properly occupied

One hole (Kramers singlet) vs. two holes vs. three holes (half-filling).

Single ion (t=0)

Δ=0

sextet $j = 5/2$, $E=2\lambda$

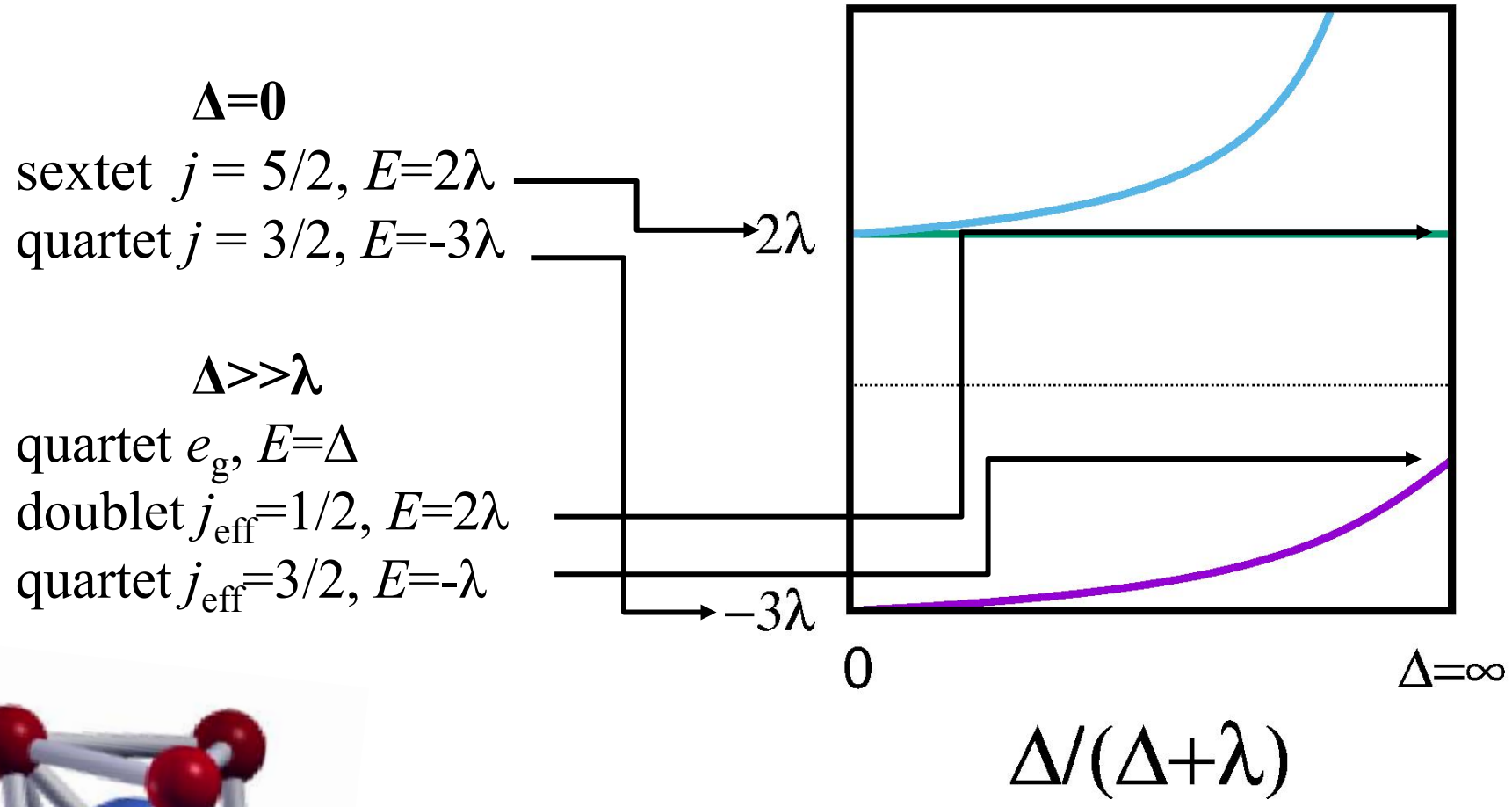
quartet $j = 3/2$, $E=-3\lambda$

Δ>>λ

quartet e_g, $E=\Delta$

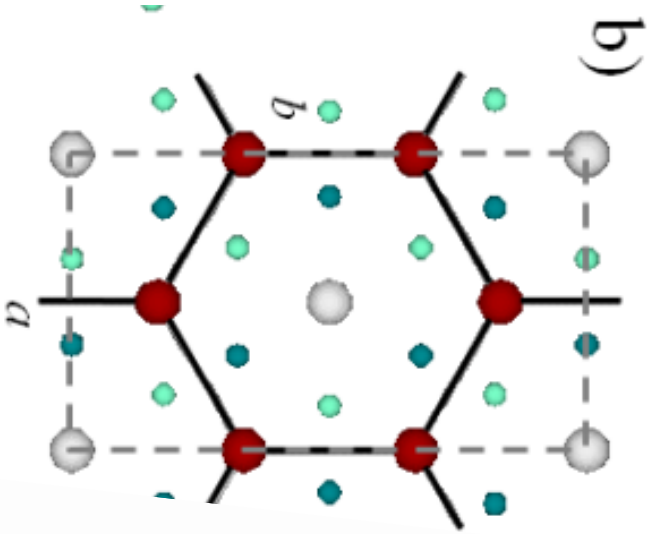
doublet $j_{eff}=1/2$, $E=2\lambda$

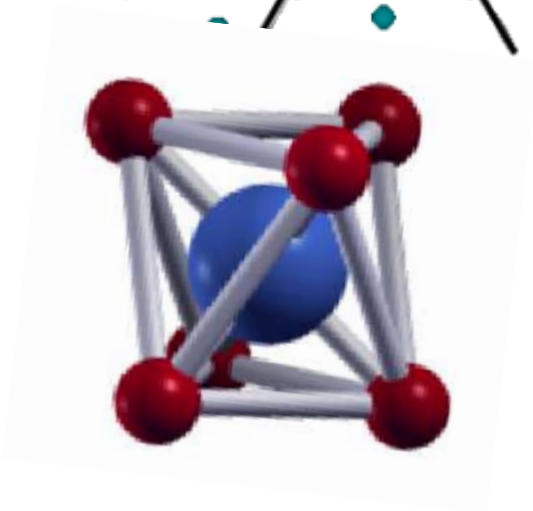
quartet $j_{eff}=3/2$, $E=-\lambda$

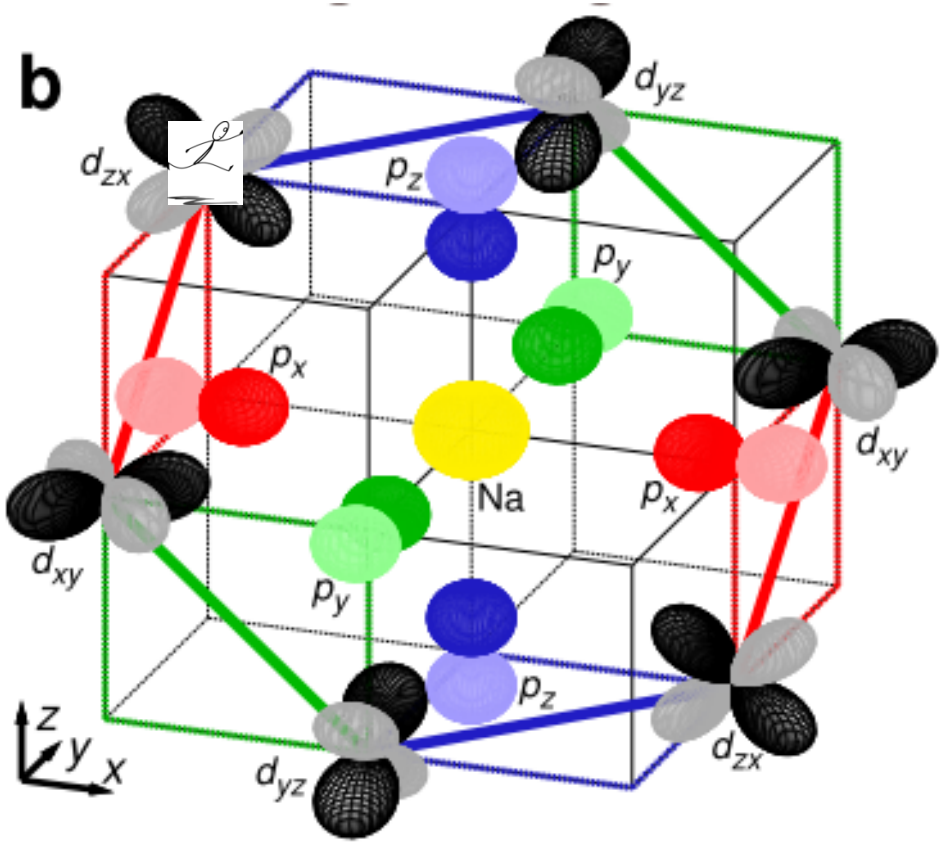


One hole in t_{2g} is *always* in a half-filled Kramers doublet -> importance of Hubbard U

Molecular orbitals





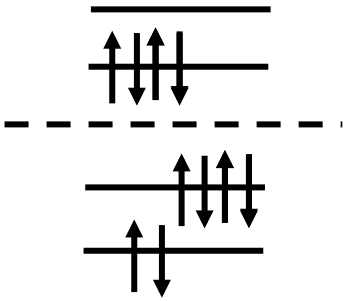


It is like an isolated benzene molecule!

Molecular orbitals: 1st approximation

We get 4 *levels*, corresponding to 2x3=6 t_{2g} orbitals.

They are occupied by 10 electrons

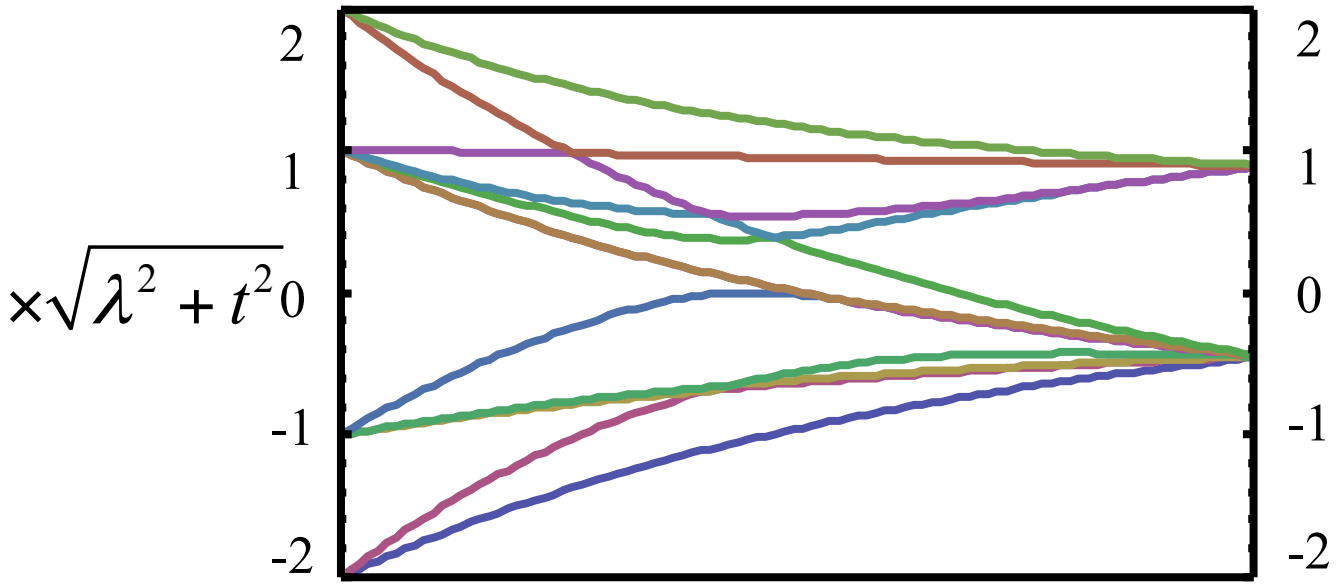


$t'_2 \sim -t'_1/3$

$\omega = \exp(i\pi/3)$

Symmetry	Eigenenergy	Eigenvector(s)
A_{1g}	$2(t'_1 + t'_2)$	1,1,1,1,1,1
E_u (twofold)	$t'_1 - t'_2$	$1, \omega, \omega^2, -1, \omega^4, \omega^5$ $1, \omega^5, \omega^4, -1, \omega^2, \omega$
E_g (twofold)	$-t'_1 - t'_2$	$1, \omega^2, \omega^4, 1, \omega^2, \omega^4$ $1, \omega^4, \omega^2, 1, \omega^4, \omega^2$
B_{1u}	$-2(t'_1 + t'_2)$	1,-1,1,-1,1,-1

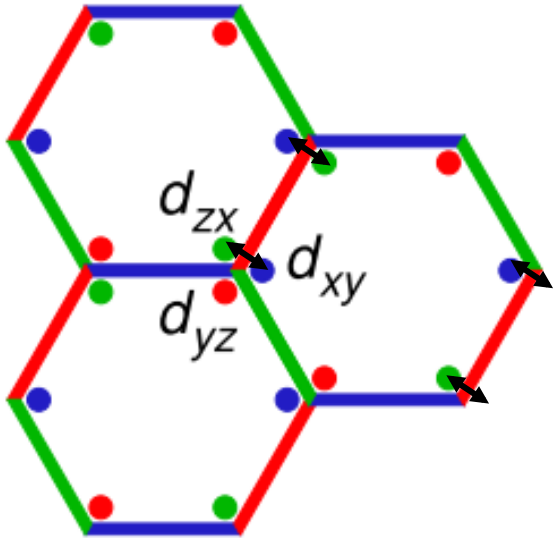
One hole in t_{2g} is *again* in a half-filled Kramers doublet!

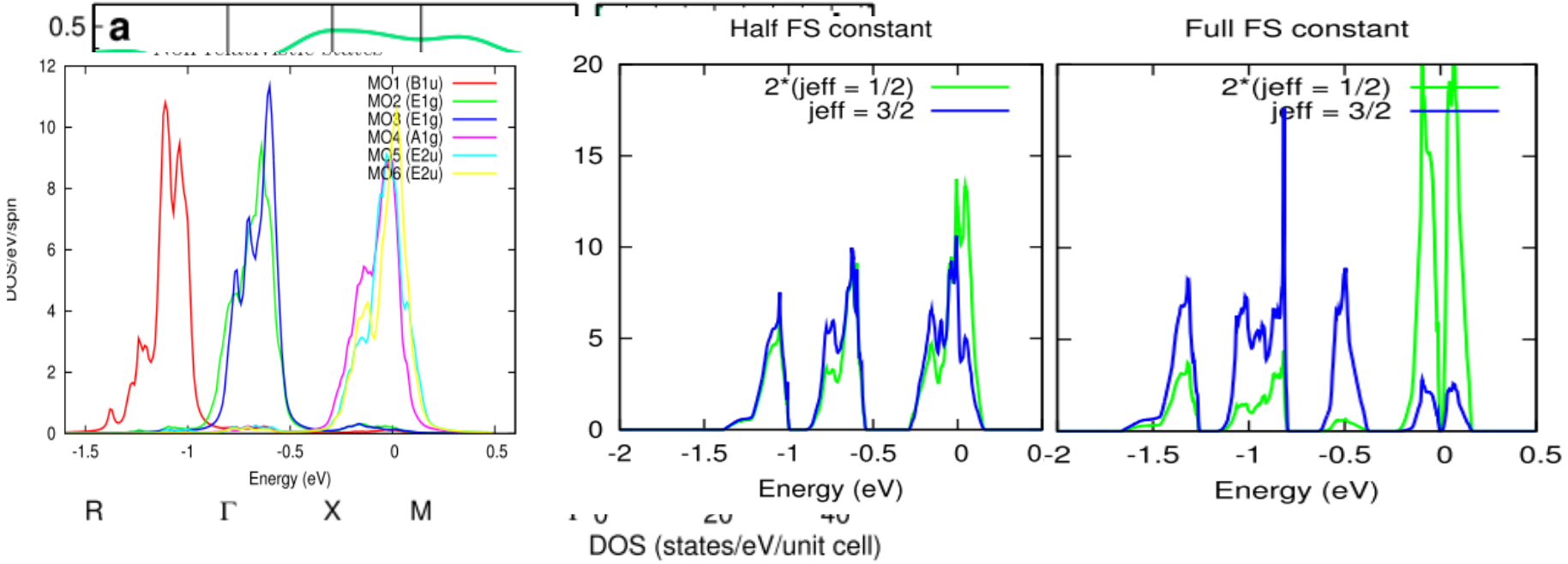


Molecular orbitals + spin-orbit

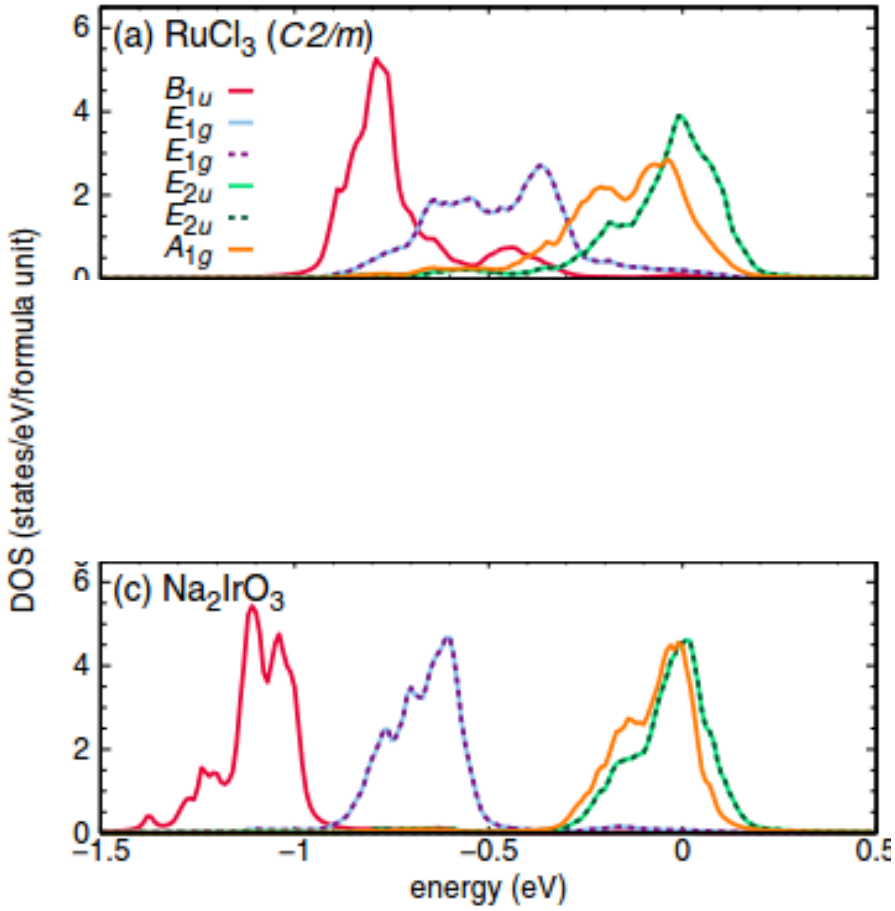
In pure molecular orbitals the spin orbit interaction is fully quenched.

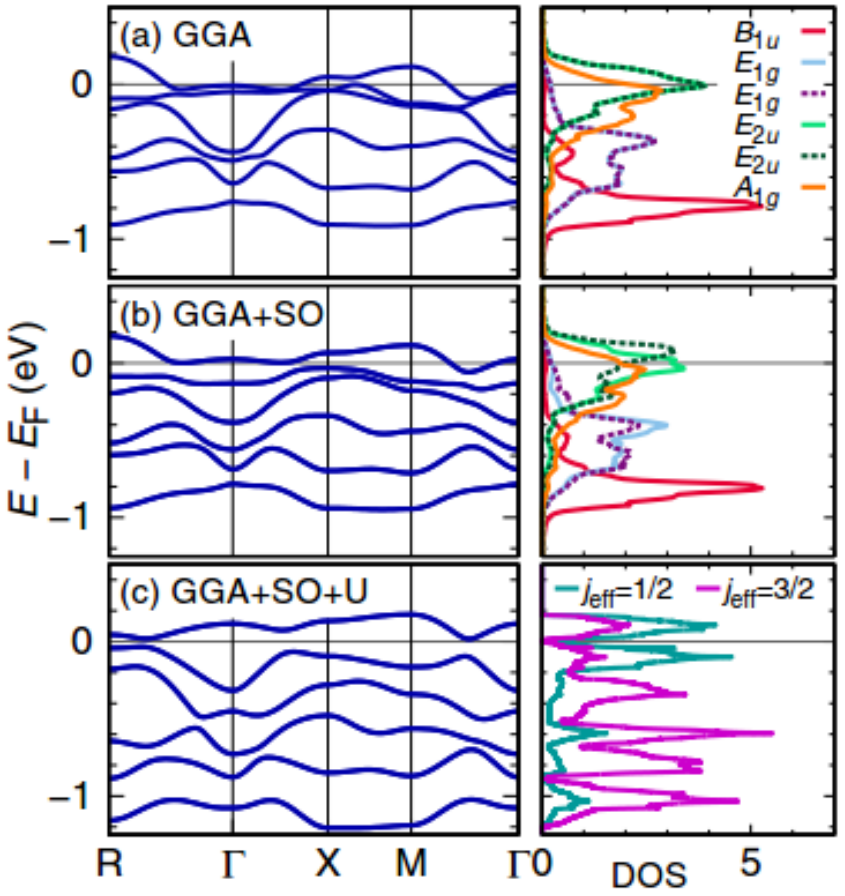
However, the upper two subbands, since they overlap, develop substantial SO-induced hybridization





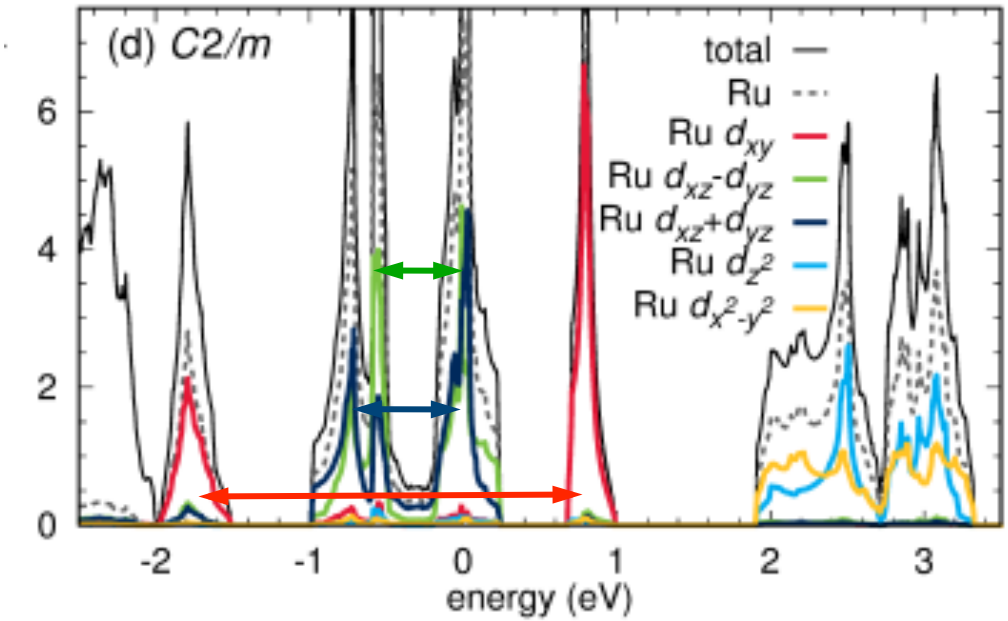
$RuCl_3$: moderate SO, still one hole

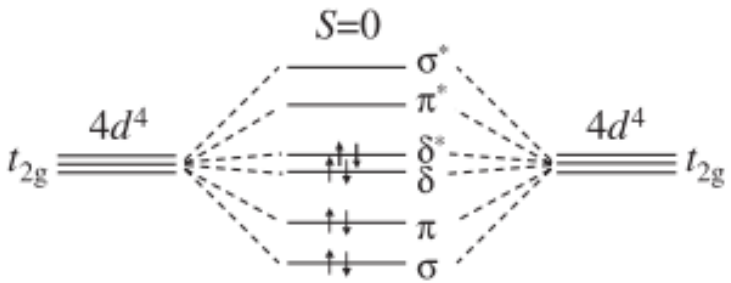




Even 3-4 times smaller SO does not prevent RO from taking over, if U singles out the KK doublet!

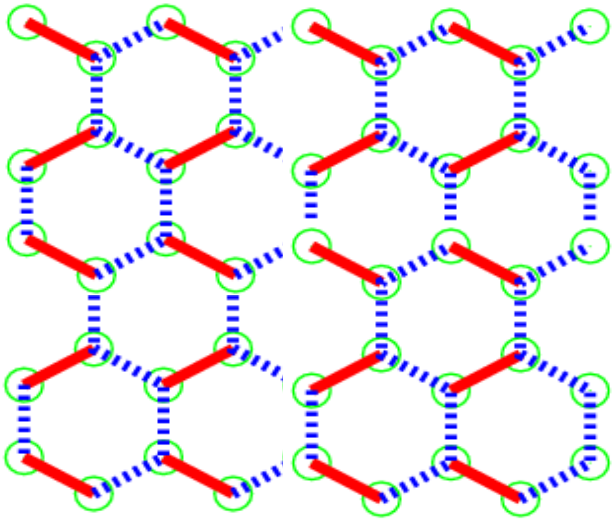
Li_2RuO_3: two holes in the KK singlet





- σ orbitals always form strong covalent bonds
- π may or may not form weaker covalent bonds

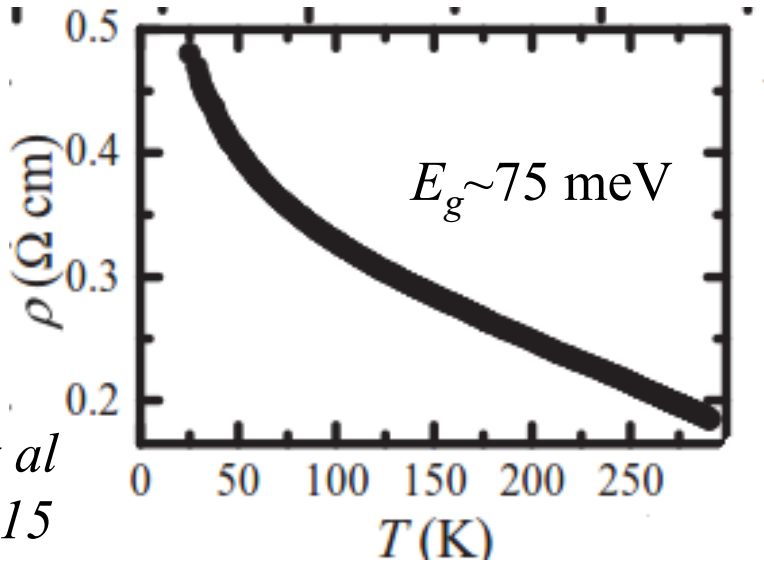
- As a result, strong dimerization occurs (20%)



Strongly MO, non-relativistic, uncorrelated $SrRu_2O_6$

EXPERIMENTAL FACTS

1. Ru^{5+} has 3 *d* electrons, *i.e.*, half-filled t_{2g}
2. Could be a Slater-Mott insulator with S=3/2 (M=3 μ_B)
3. Measured M=1.3-1.4 μ_B (55%); hybridization suppression in other ruthenates is <30% (in metals) or a few % (in insulators)
4. Very high for a strongly 2D material T_N~560 K
5. Barely semiconducting behavior



Hiley et al
PRB 2015

Strongly MO, non-relativistic, uncorrelated $SrRu_2O_6$

COMPUTATIONAL FACTS COROLLARIES

1. Only Neel state stable (not a single FM bond can be stabilized!)

   Magnetic interactions are strongly non-Heisenberg; weak correlations

2. Calculated moment exactly agrees with the experiment

   Confirms that correlations are weak

3. Fully insulating without magnetism, despite half-filling

   Opens a *covalent-type* gap without any dimerization

4. The gap (no correlation corrections) is ~400 meV, too large (!)

   Confirms weak correlations once again

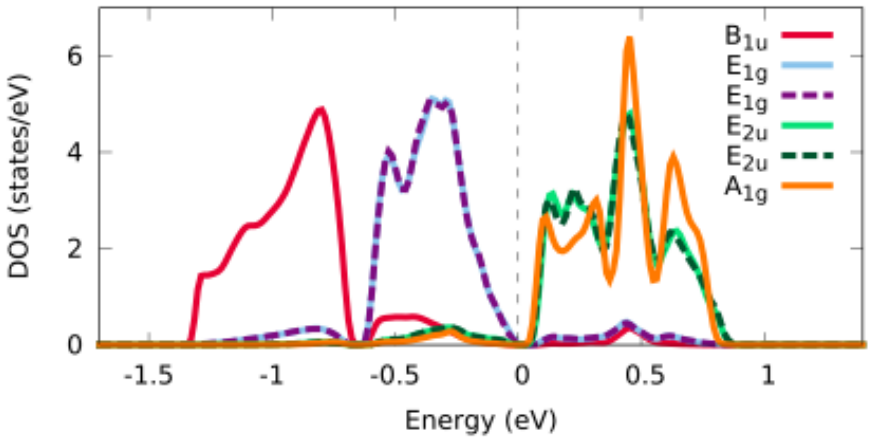
5. Interlayer coupling is ~1.5 meV, anisotropy ~1.4 meV

   n.n. antiferromagnetic coupling must be extremely strong (>1500 K)

Principal questions:

1. Why ferromagnetism is impossible (gap?)
2. Why gap?
3. Why AFM so strong (weak correlations?)
4. Why weak correlations?

All answers provides by MOs



- SO hardly changes anything
- Electrons are *highly delocalized* over hexagons, but MO are *highly localized*

CONCLUSIONS

- Structurally similar honeycomb 4d and 5d compounds behave totally different, depending of whether they have 1, 2, or 3 t_{2g} holes
- One hole promotes SO effects; Hubbard U is a requisite for 4d, but not 5d
- Two holes strive to form dimers, kill both SO+U and molecular orbital effects
- Three holes gain large covalent advantage from forming MOs
- $SrRu_2O_6$ is a perfect example of a MO solid, and thus has unique magnetic properties: there is considerable *penalty* for creating local moments, but if the latter *are* created, they are stabilized by enormous AF n.n. interaction, *also* driven by MOs!

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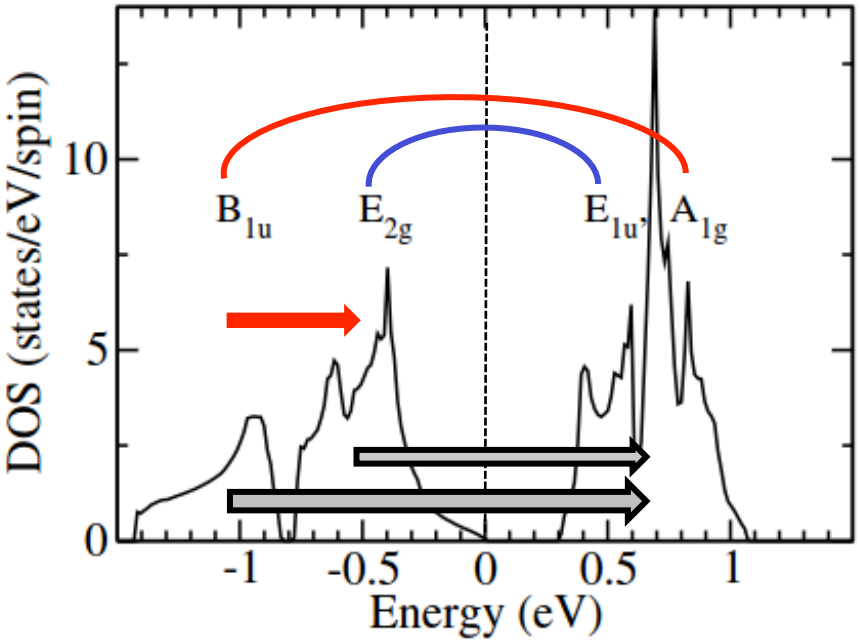
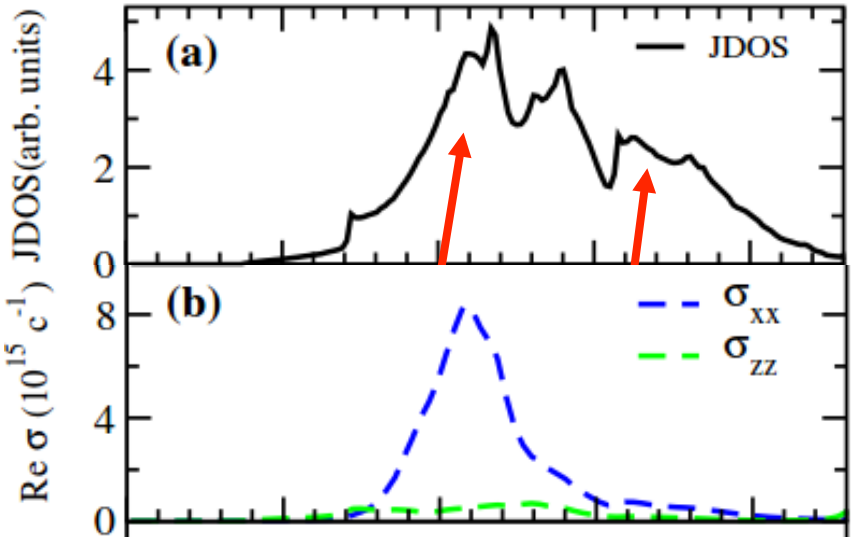
Localized itinerant electrons and unique magnetic properties of $SrRu_2O_6$

Direct experimental test: optics





$$\mathrm{Im}\ \varepsilon_{\alpha\beta}(\omega) = \frac{e^2}{\pi m^2 \omega^2} \sum_{c,v} \int \langle c,\mathbf{k}|p^{\alpha}|v,\mathbf{k}\rangle\langle v,\mathbf{k}|p^{\beta}|c,\mathbf{k}\rangle \times \delta(\epsilon_c(\mathbf{k}) - \epsilon_v(\mathbf{k}) - \hbar\omega) d\mathbf{k}. \quad (5)$$

$$J(\omega) = \sum \int \delta(\epsilon_c(\mathbf{k}) - \epsilon_v(\mathbf{k}) - \hbar\omega) d\mathbf{k},$$

$$B_{1u} \times A_{1g} = B_{1u}$$
$$B_{1u} \times E_{2g} = E_{1u}$$
$$E_{2g} \times E_{1u} = B_{1u} + B_{2u} + E_{1u}$$
$$E_{1u} \times A_{1g} = E_{1u}$$

$P_{x,y}$

Nontrivial behavior of matrix elements is a direct consequence of molecular orbitals!

WE NEED U!

Orbital occupation

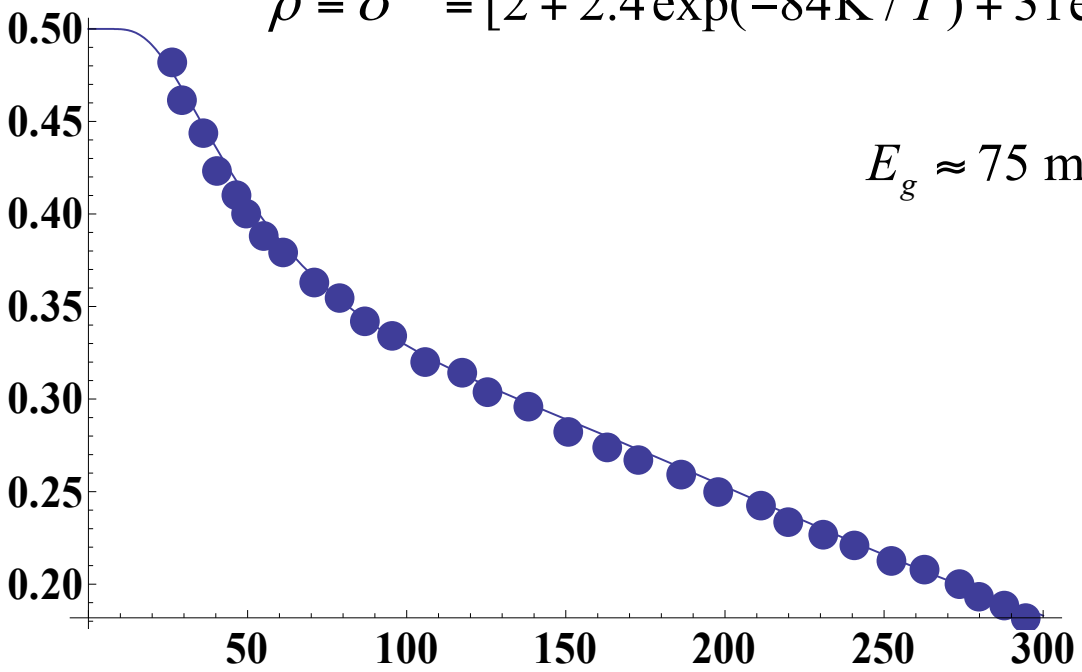
Spin-orbit

Molecular orbitals

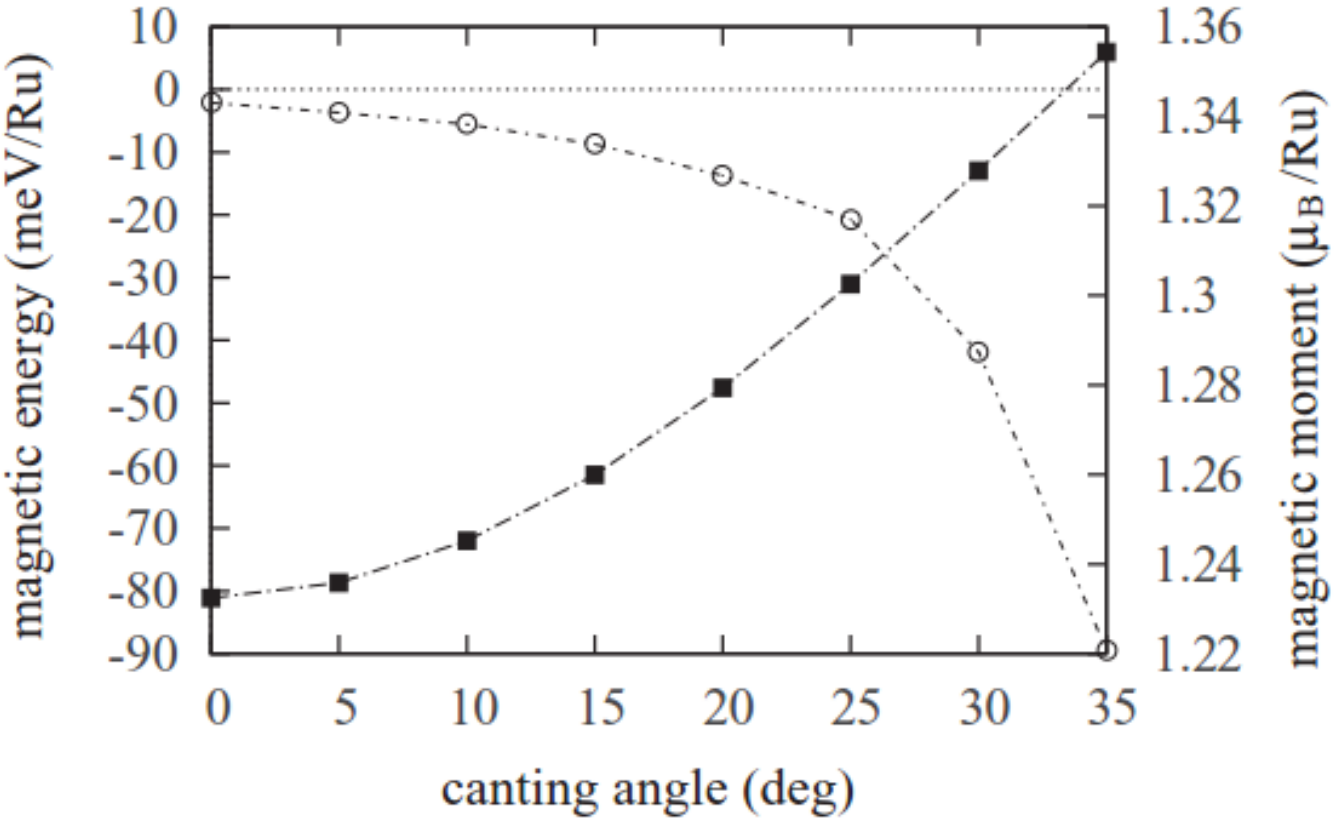
God did not make all men equal. U ~~Colonel Colt~~ did.

End of the talk

$$\rho = \sigma^{-1} = [2 + 2.4\exp(-84\text{K}/T) + 31\exp(-880\text{K}/T)]^{-1}\ \Omega\ \text{cm}$$



$$E_g \approx 75\ \text{meV}$$


magnetic energy (meV/Ru)
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
0
5
10
15
20
25
30
35
canting angle (deg)
1.36
1.34
1.32
1.3
1.28
1.26
1.24
1.22
magnetic moment (μB /Ru)