Can we understand the high-Tc superconducting cuprates from first principles?

Lucas K. Wagner

ILLINOIS

Outline

Can FN-DMC obtain accurate results on transition metal oxides?

What's the difference between DFT and the FN-DMC solution?

Are the cuprates special in any way compared to the other transition metal oxides?

What new physics can we learn from better simulations?

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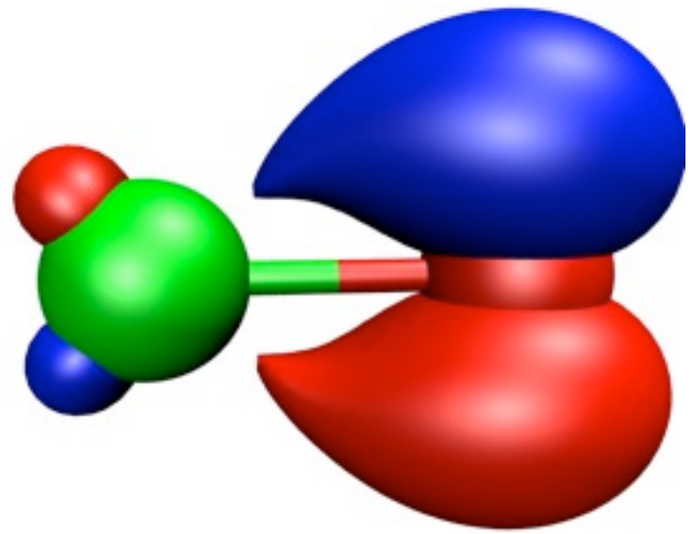
Complex relationship between spin and lattice

Code: QWalk

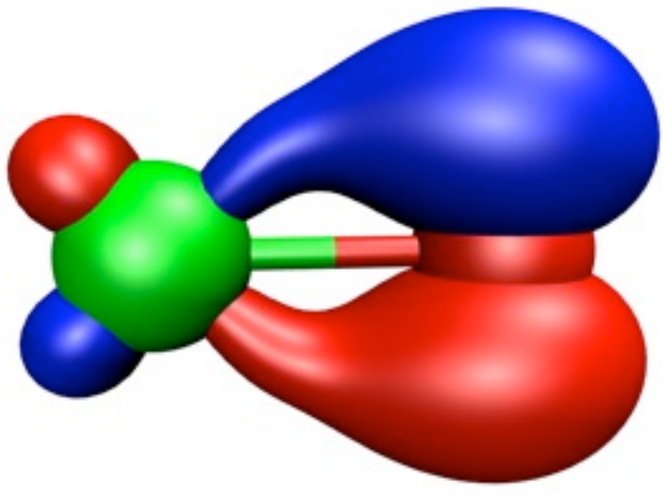
- Fairly easy to compile and use
- Very good at using localized basis, but can use blips
- Full-featured: PBCs, RMC
- ~130 people on mailing list
- http://qwalk.org

Why does correlation matter for d-p hybridization?

Interaction of localized and delocalized states.
Relative energetics highly dependent on treatment of correlation



Hartree-Fock

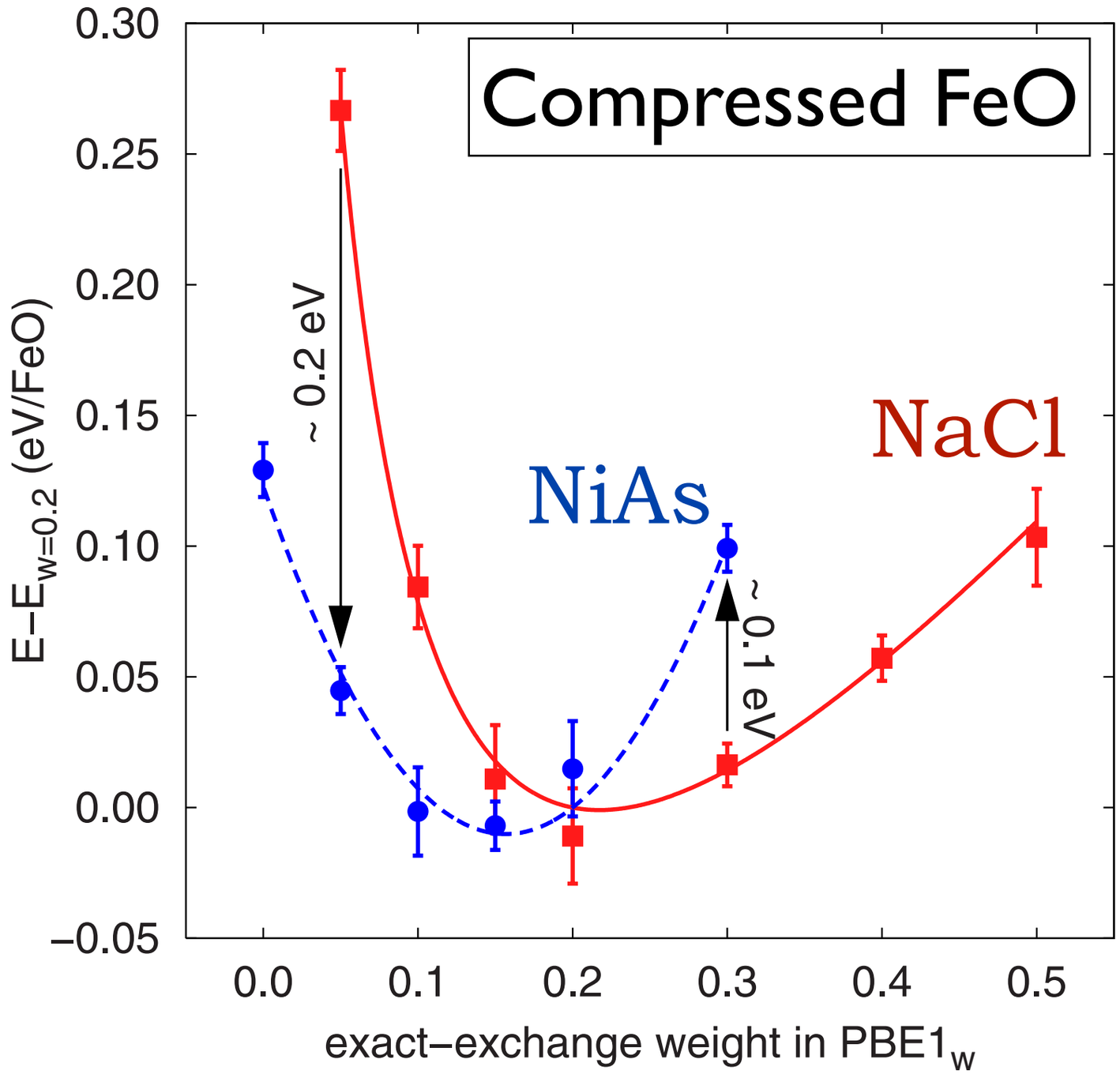


Hybrid DFT

LDA: too much delocalization
HF: too little delocalization

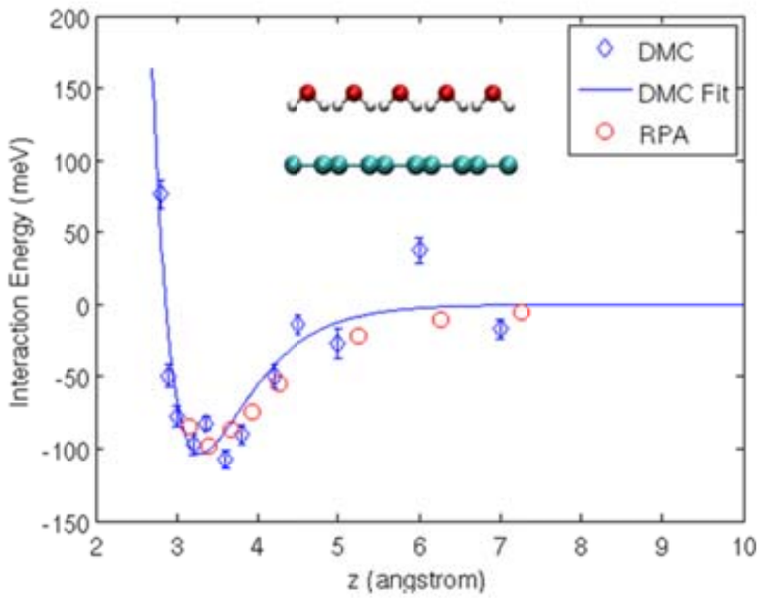
Wagner & Mitas, Chem. Phys. Lett. 370 412 (2003)
Wagner & Mitas, J. Chem. Phys. **126,** 034105 (2007)

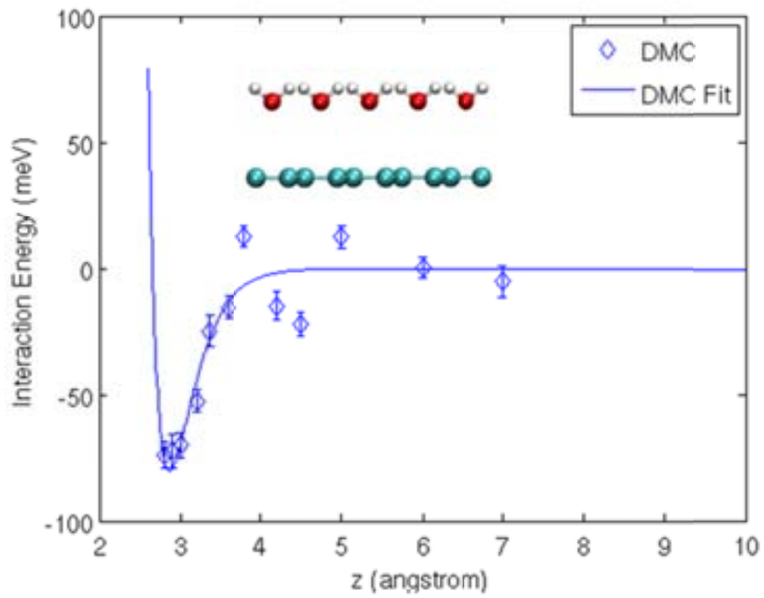
Importance of d-p hybridization in the nodes

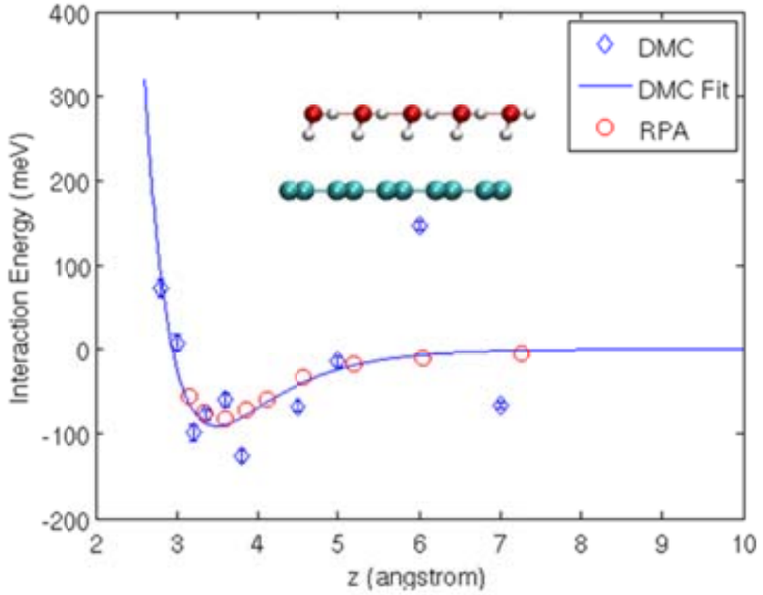


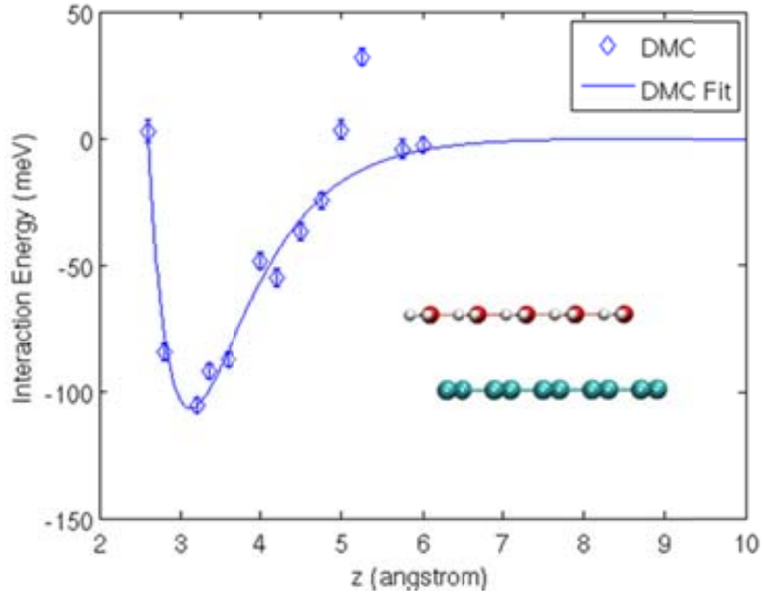
Kolorenc, Hu, and Mitas, Phys. Rev. B 82, 115108 (2010)

Water interacting with graphene









Estimated contact angle <40°

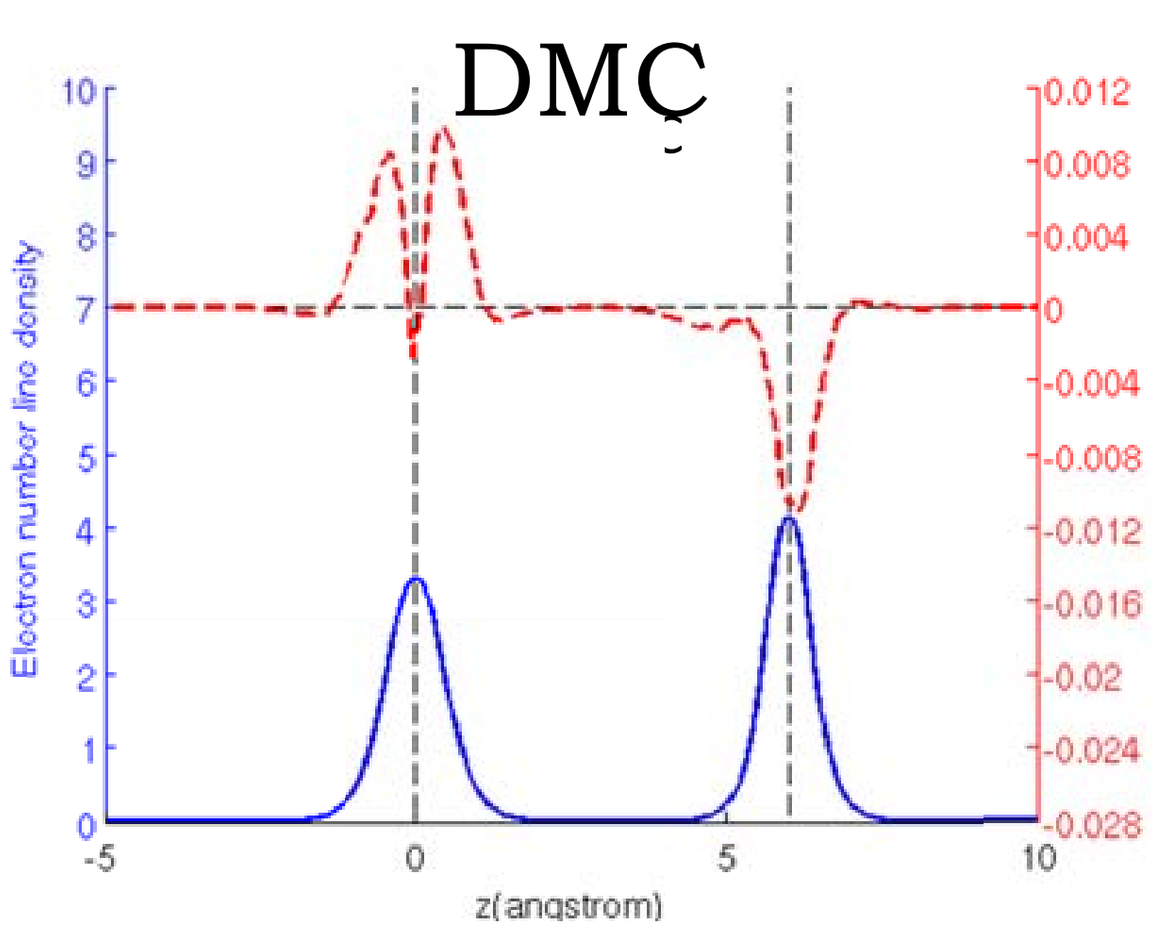
Most experiments: ~90°

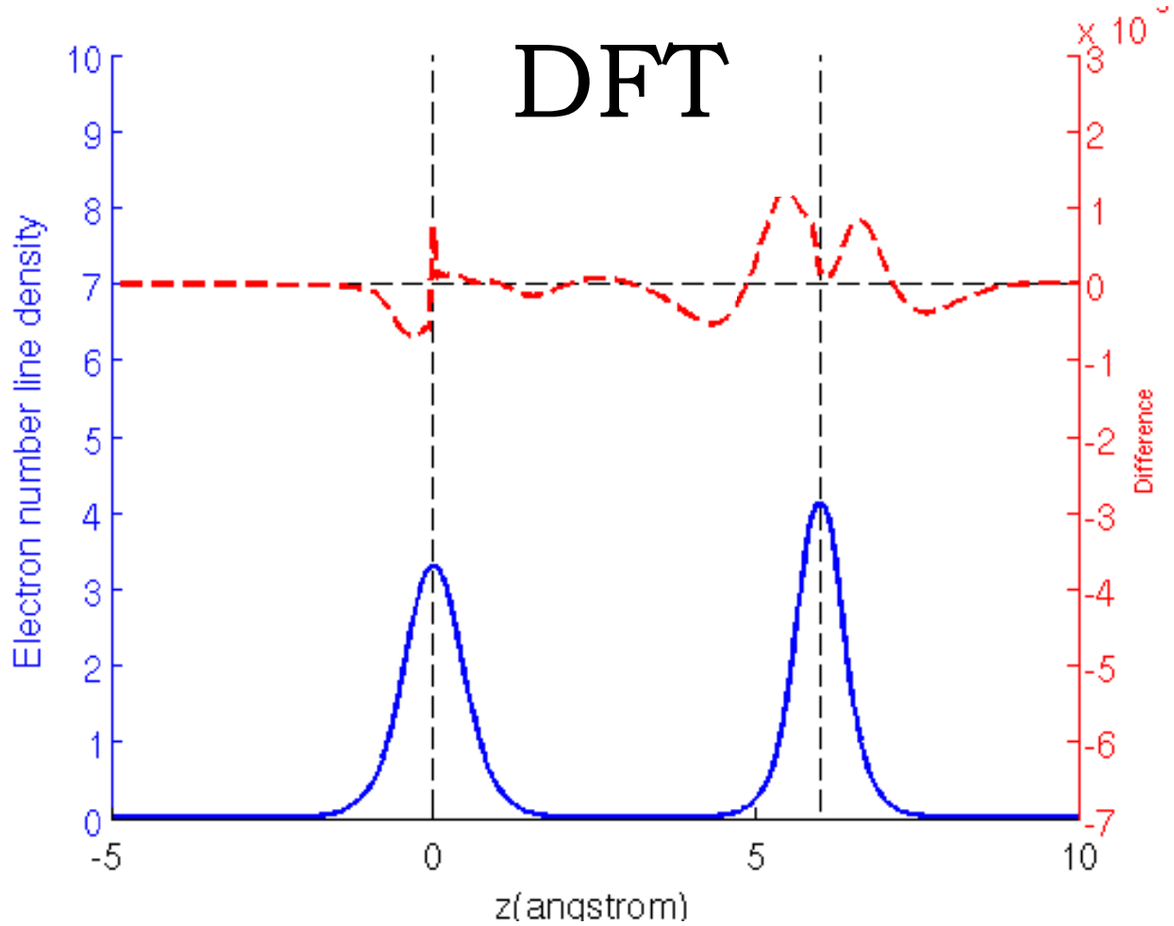
New experiment: 40°

Yanbin Wu, Wagner, Ceperley, Aluru (in preparation)

Li, et al. Nat. Mat. 2013 (advanced pub)

Charge transfer errors





A major error of DFT is the misprediction of the charge transfer, even at long distances.

Yanbin Wu, LKW, D.M. Ceperley, N. Aluru (in preparation)

LDA+U

p-band

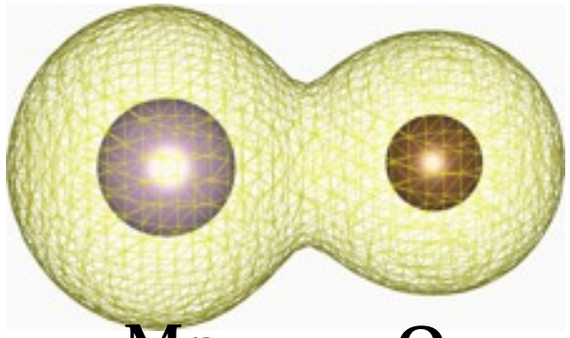
upper Hubbard band

lower Hubbard band

LDA

LDA+U

2-particle deviations from Slater det



Antibonding

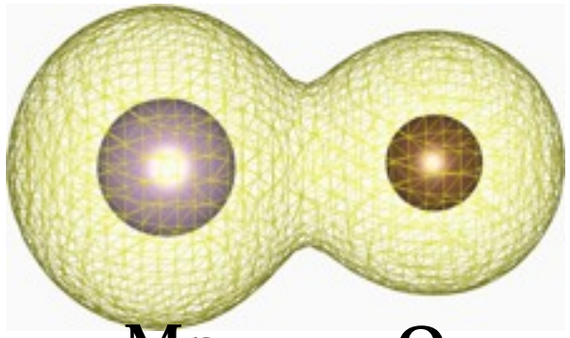
Semi-local d-like orbitals

Bonding orbitals

		σ^*
		π^*
		π^*
		σ^*
		δ
		δ
		π
		π
		σ
Majority	Minority	

Nominal ground state

2-particle deviations from Slater det



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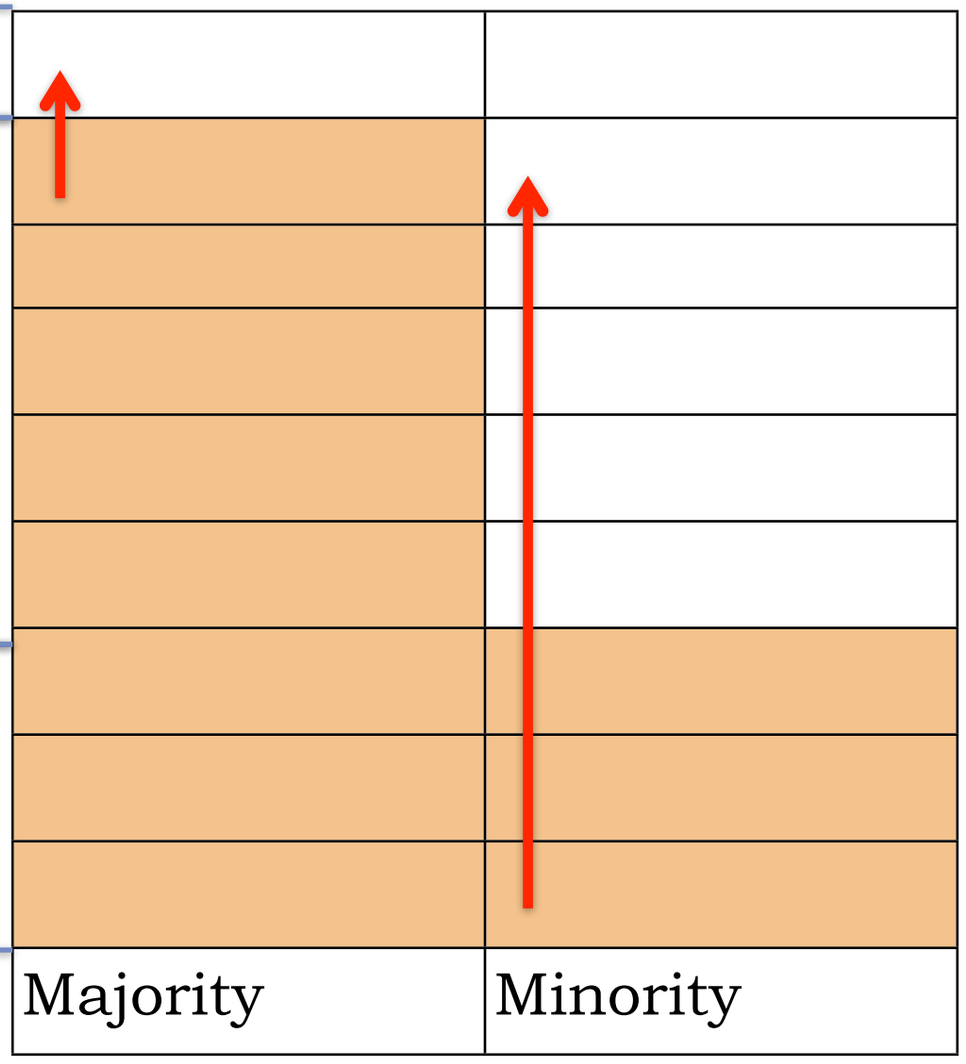

σ^*
π^*
π^*
σ^*
δ
δ
π
π
σ

Nominal ground state

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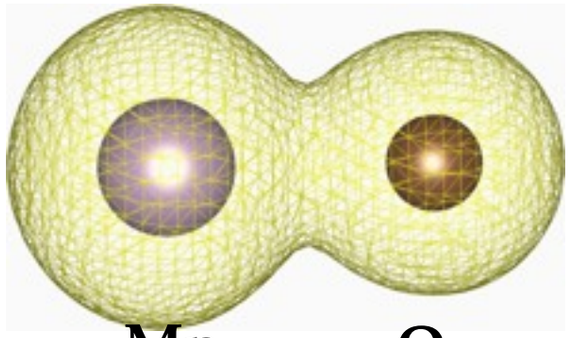

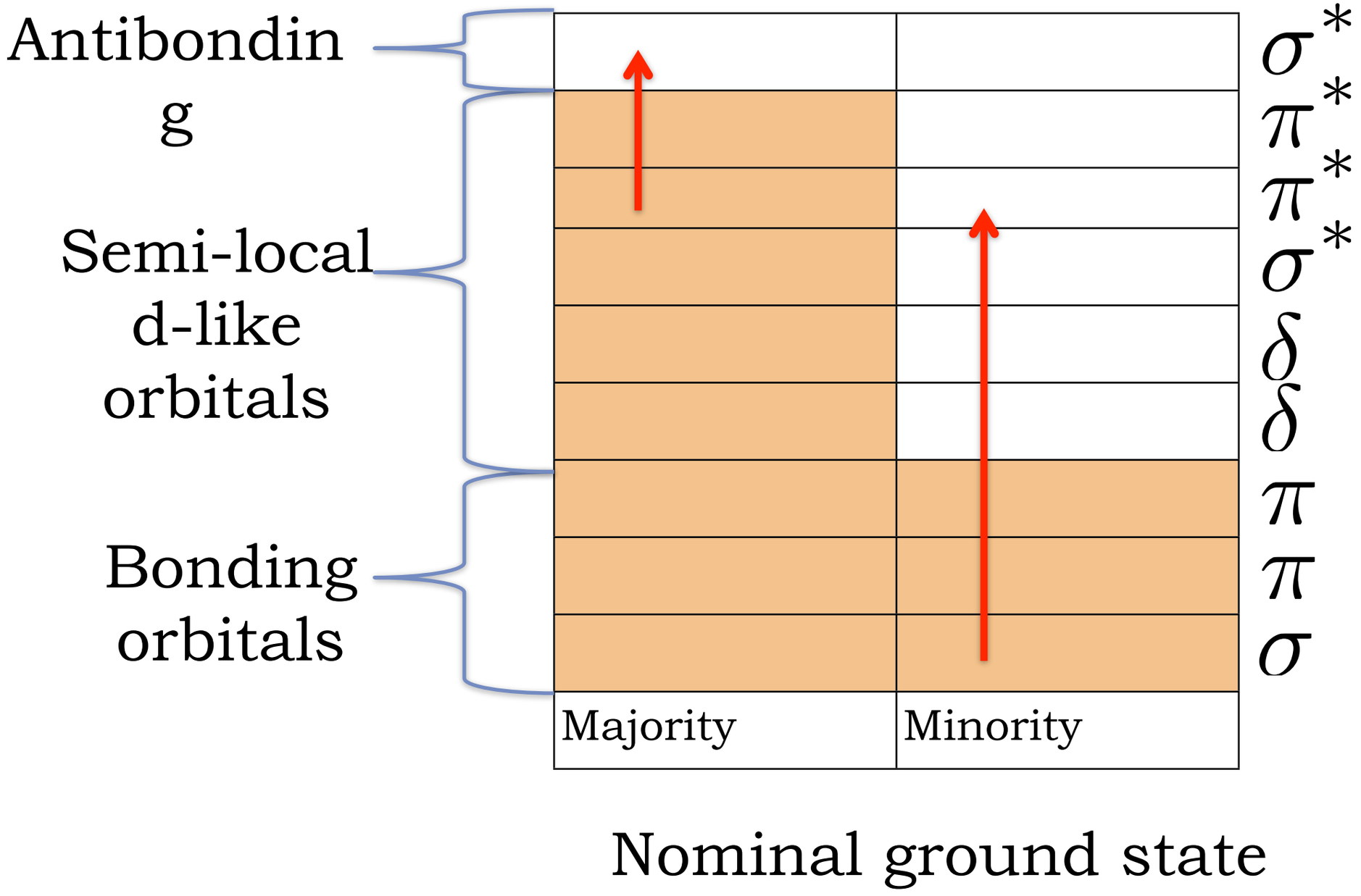

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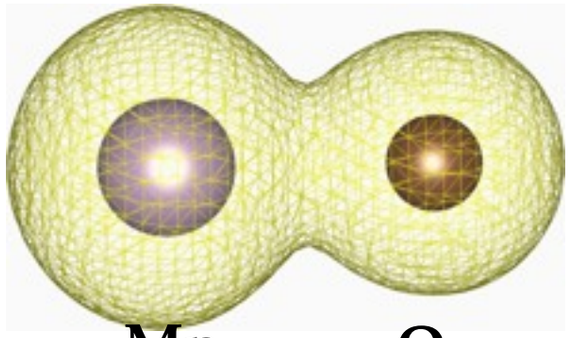

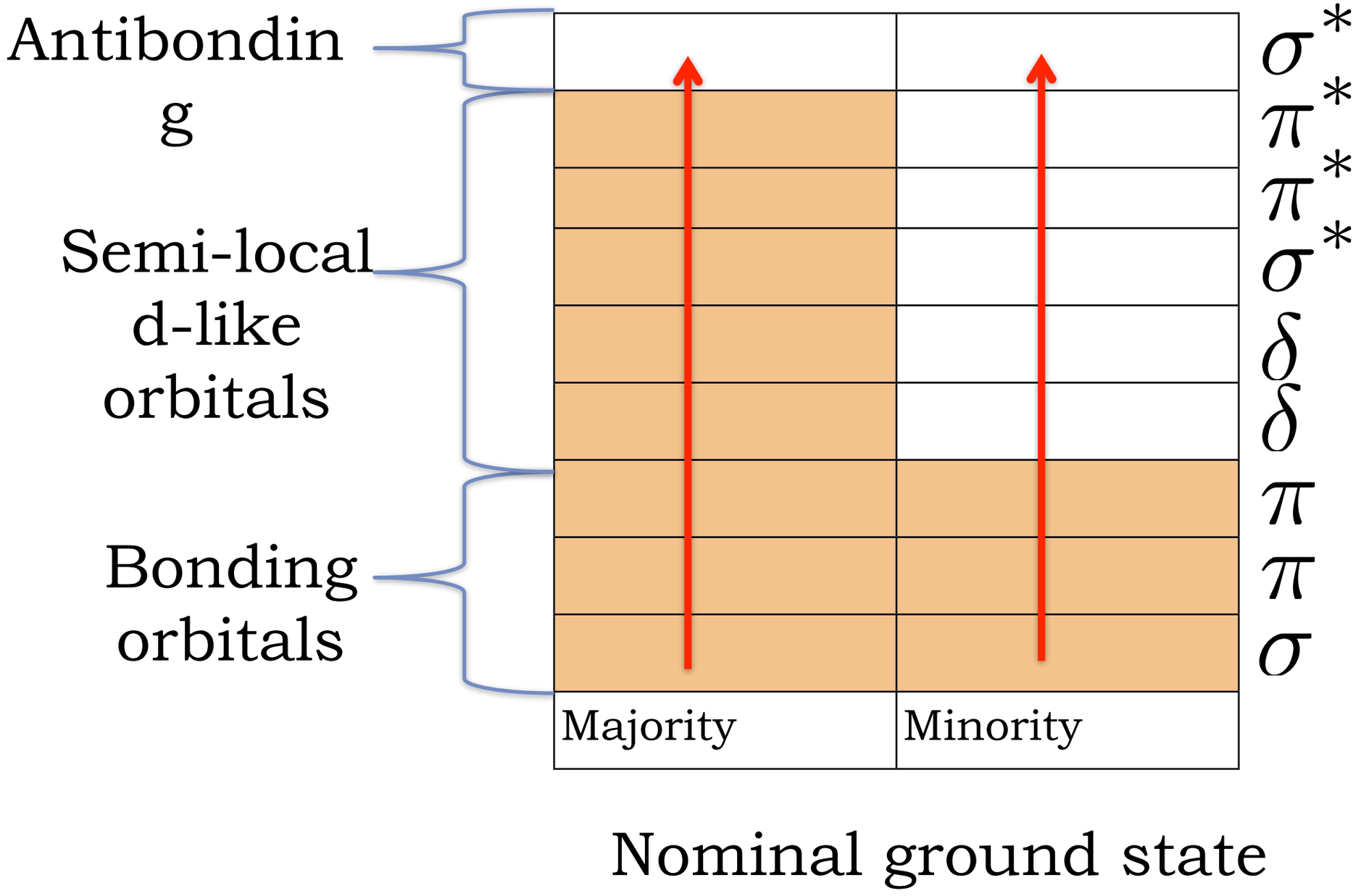

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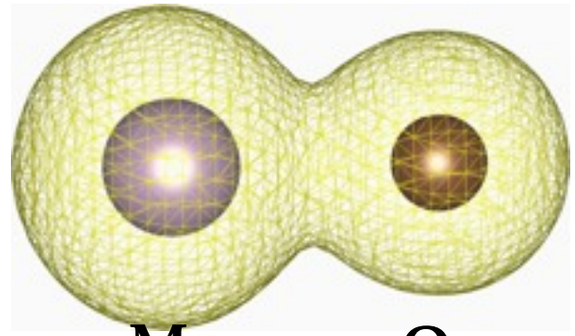
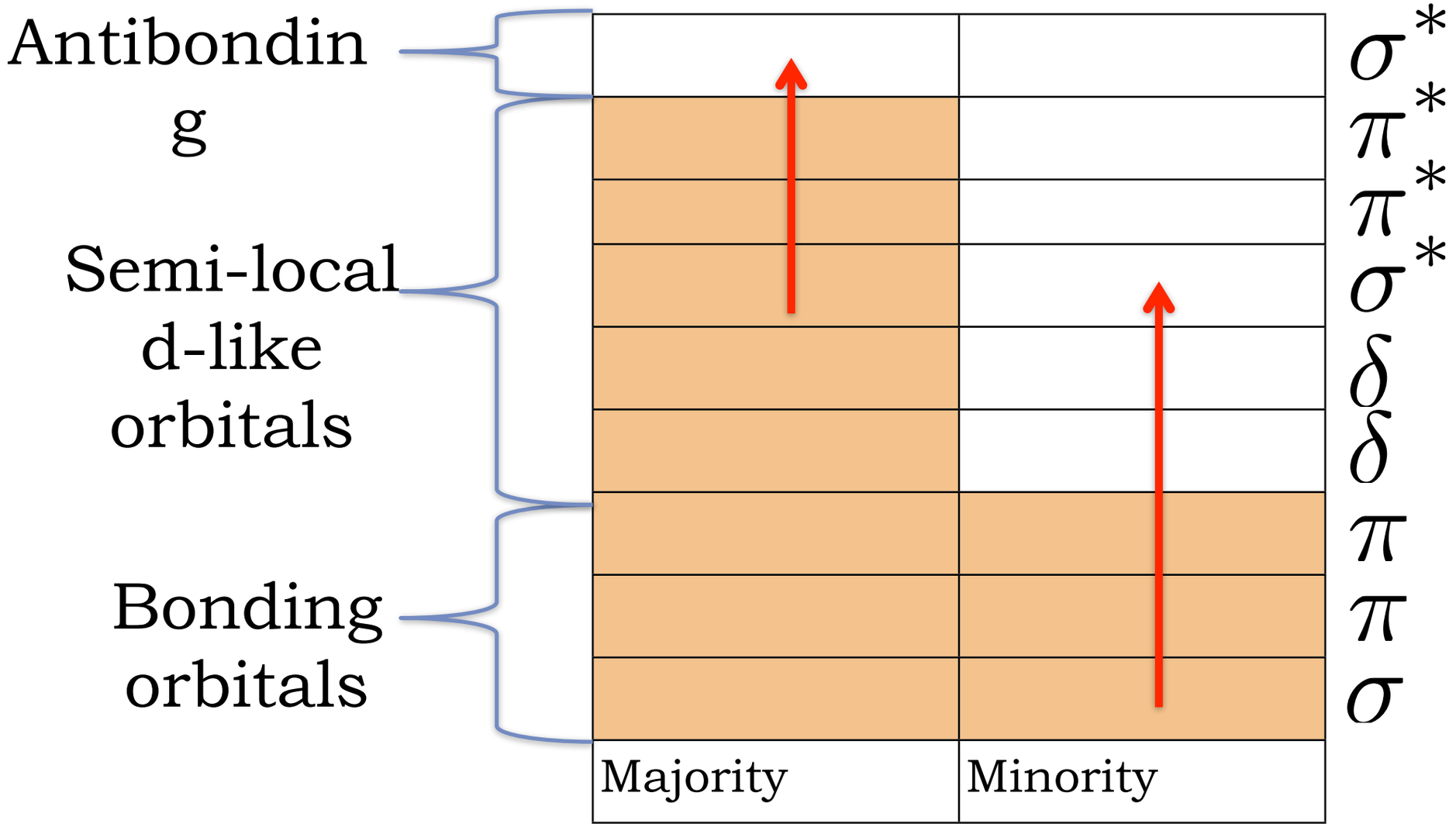
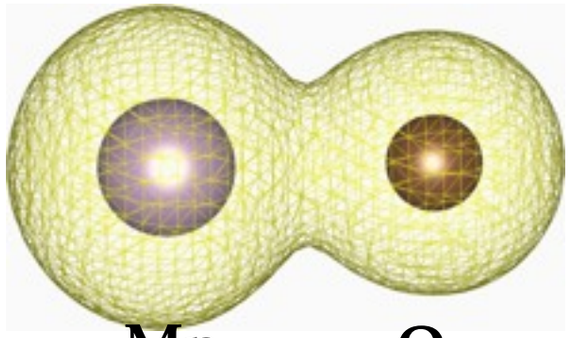
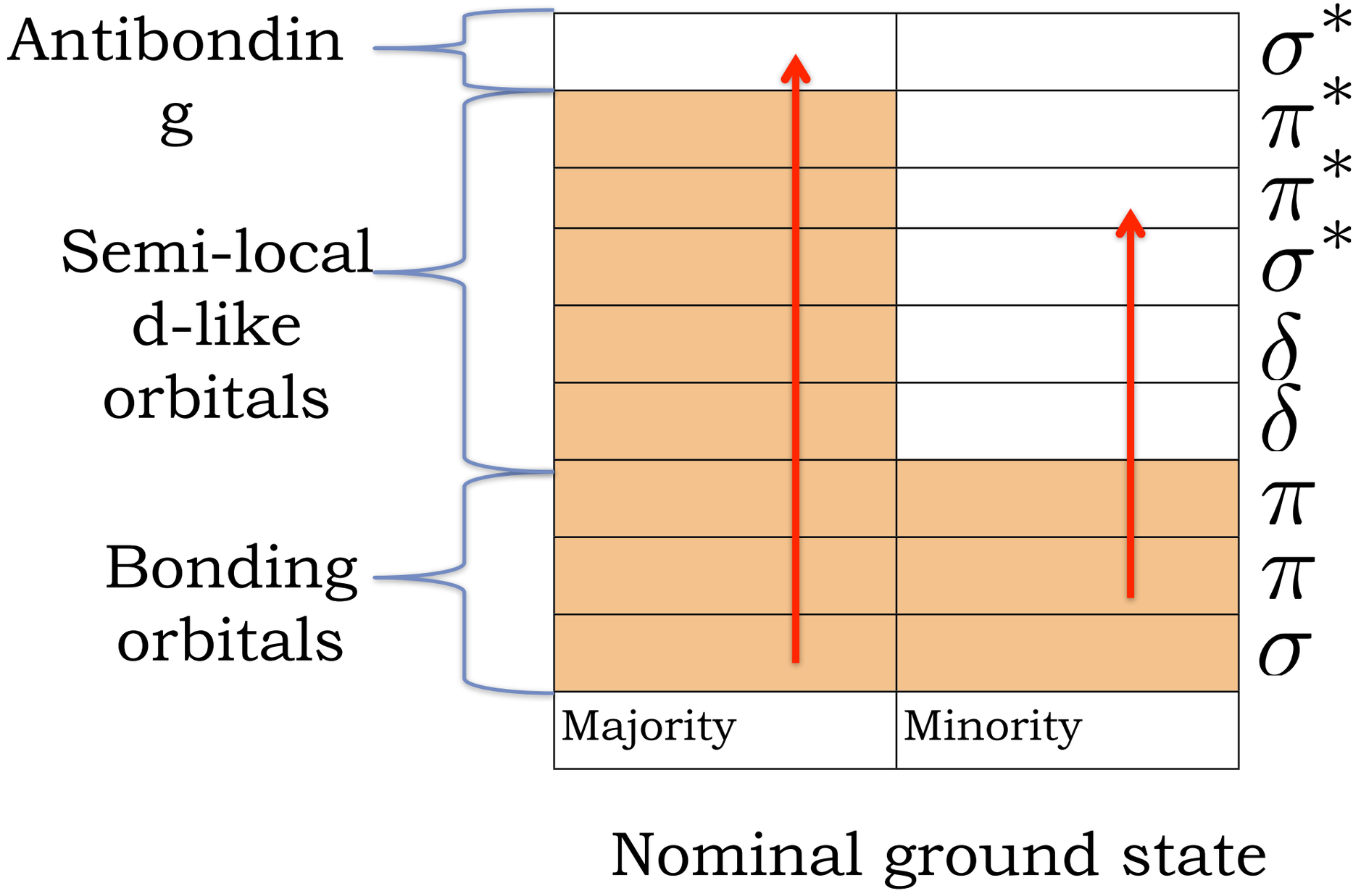




Nominal ground state

2-particle deviations from Slater det





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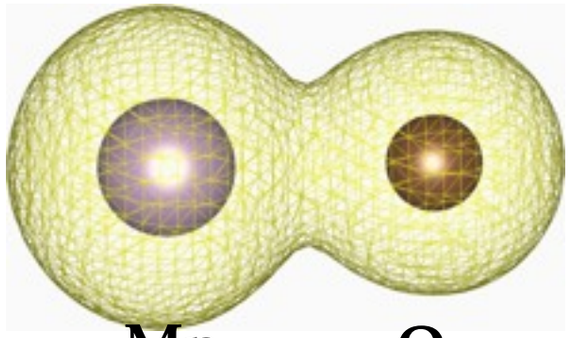
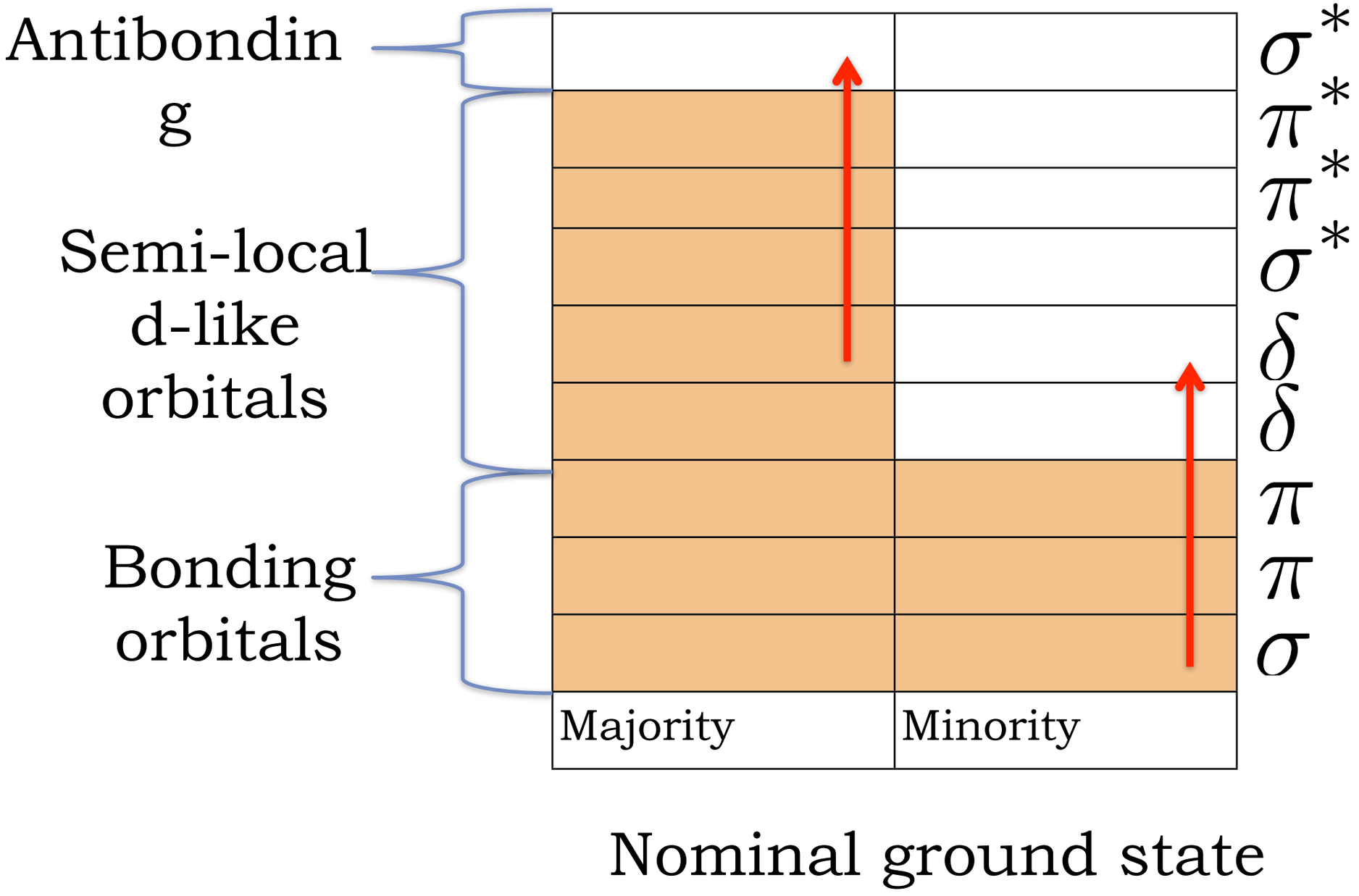
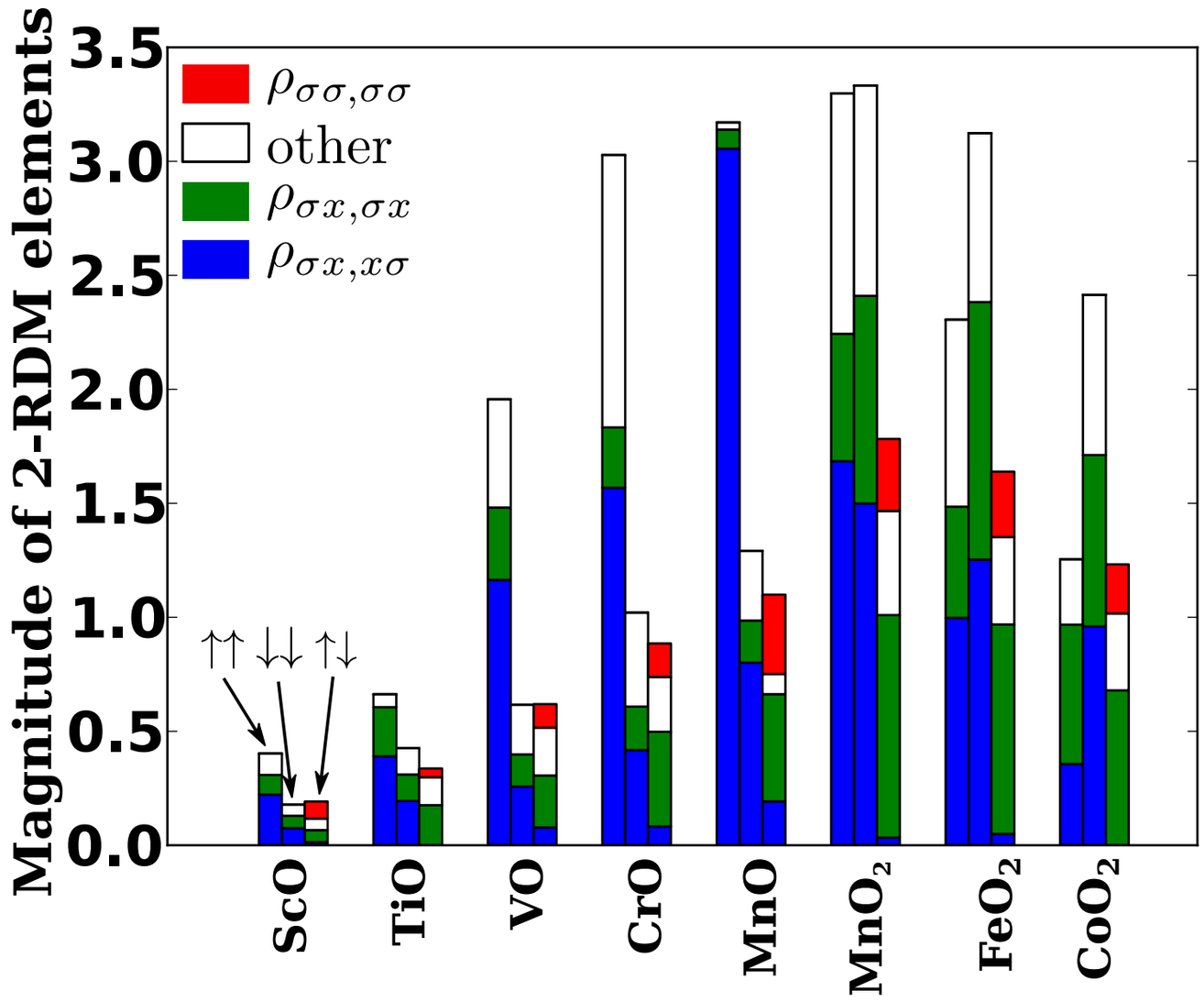




Nominal ground state

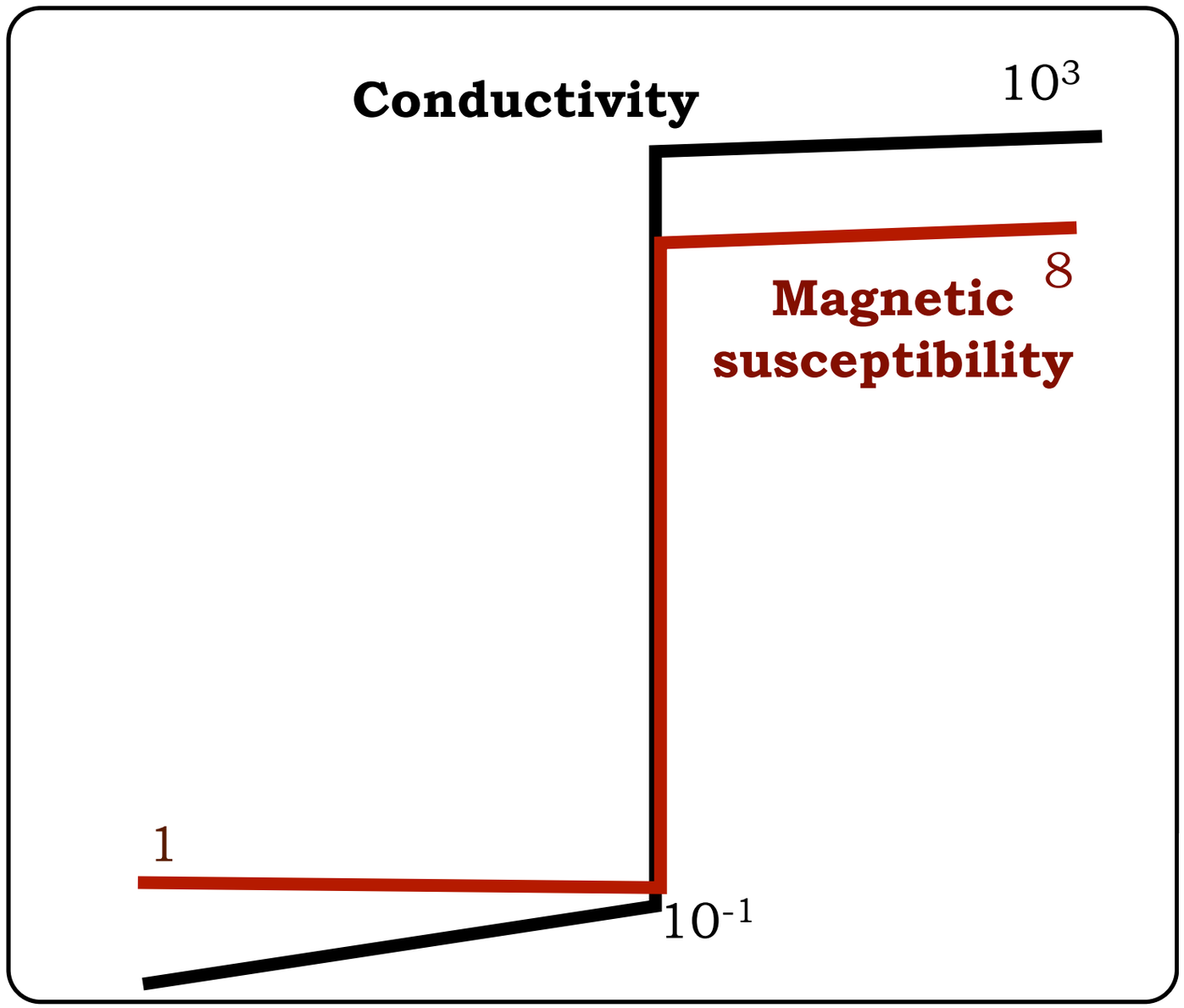
Why on-site correlation doesn't always work

Blue/green are off-diagonal elements of the 2-RDM that cannot be replicated to on-site Hubbard U type parameters

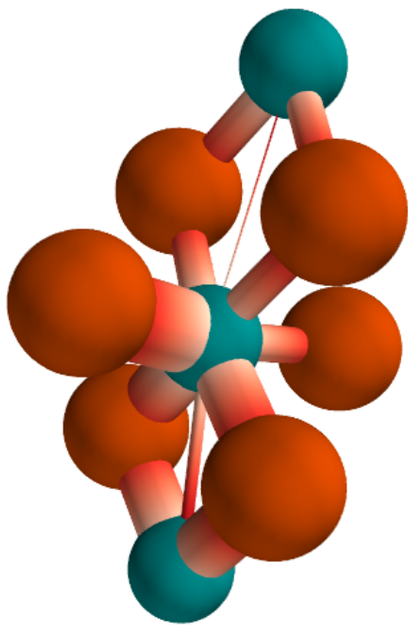


LKW, J. Chem. Phys. **138**, 094106 (2013)

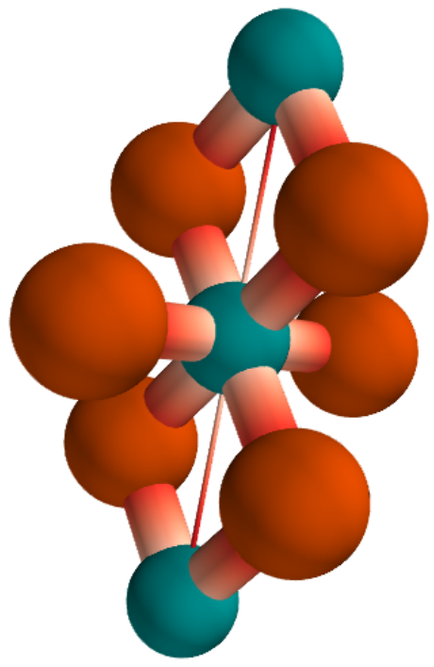
A simpler transition: VO_2



Monoclinic



Rutile



after Berglund and Guggenheim. Phys. Rev. 185 1022 (1969)

Qualitative description of VO_2

	Rutile	Monoclinic
Experiment	Metallic Paramagnetic Higher energy	Insulating Nonmagnetic Lower energy
LDA/GGA	Metallic	Metallic
Hybrid DFT	Metallic Lower energy	Insulating Higher energy
DFT+U	Insulating	Insulating
FN-DMC	Metallic Paramagnetic Higher energy	Insulating Nonmagnetic Lower energy

Huihuo Zheng, LKW (in preparation)

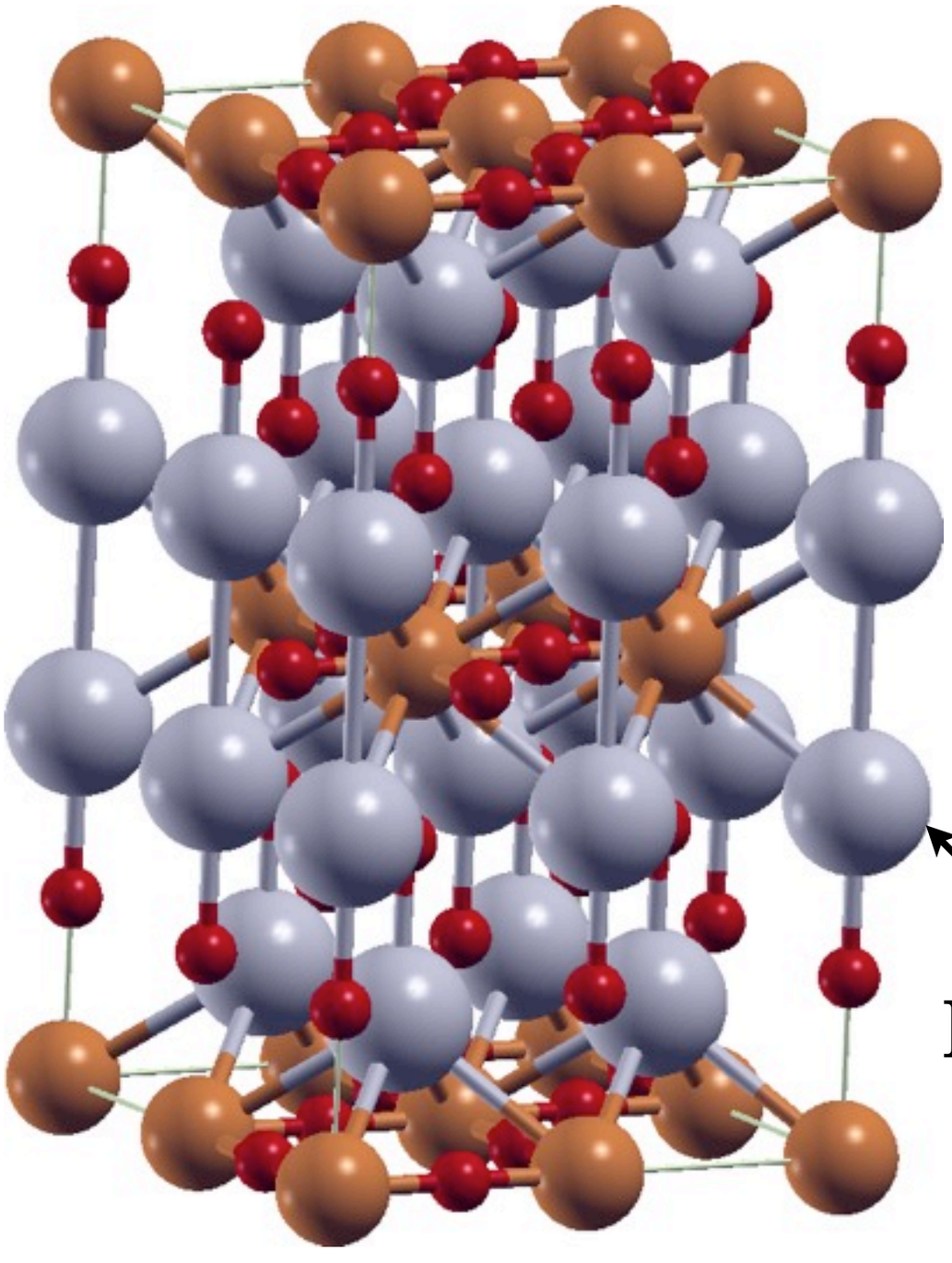
Summary so far

The problem of “strong correlation” is closely related to the problem of accurately simulating both localized/ delocalized systems.

This appears particularly strongly in the d-p hybridization.

On-site effective potentials can hack in a fix, but cannot describe all correlations accurately.

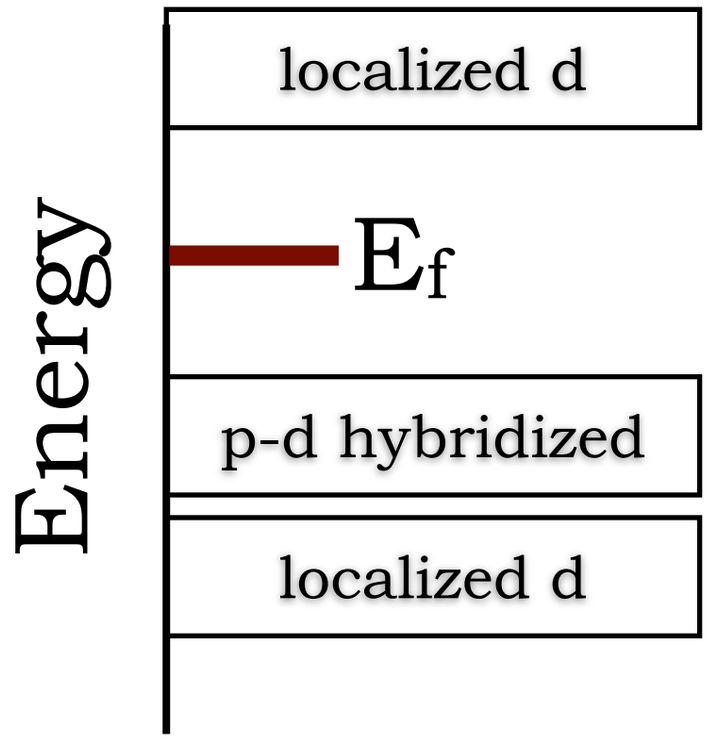
$La_{2-x}Sr_xCuO_4$ (LSCO) crystal structure



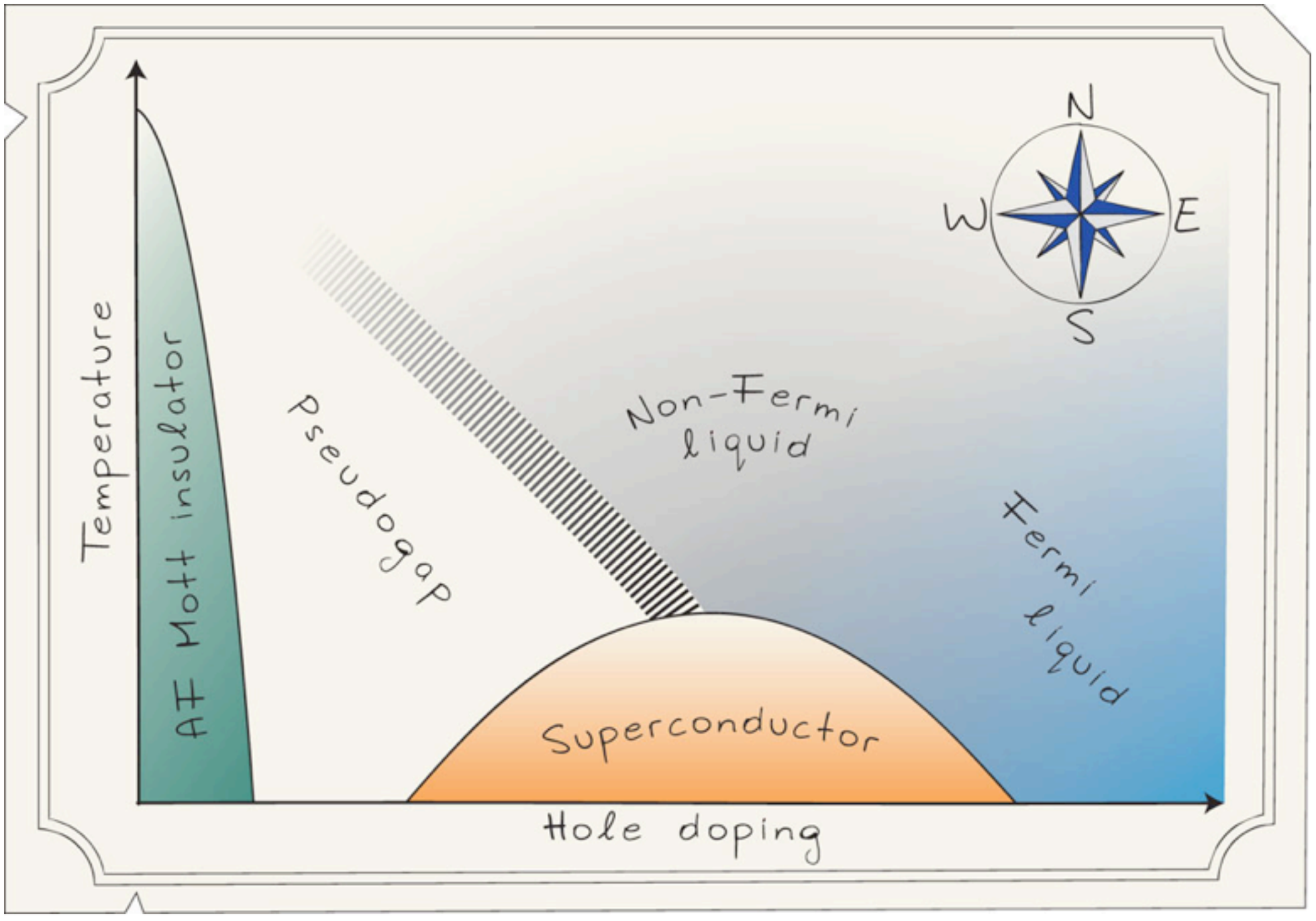
CuO_2 plane

LaO 'spacer'

Doping: La-> Sr



Basics of cuprates: phase diagram



Peter Wahl. Nature Physics 8, 514–516 (2012)

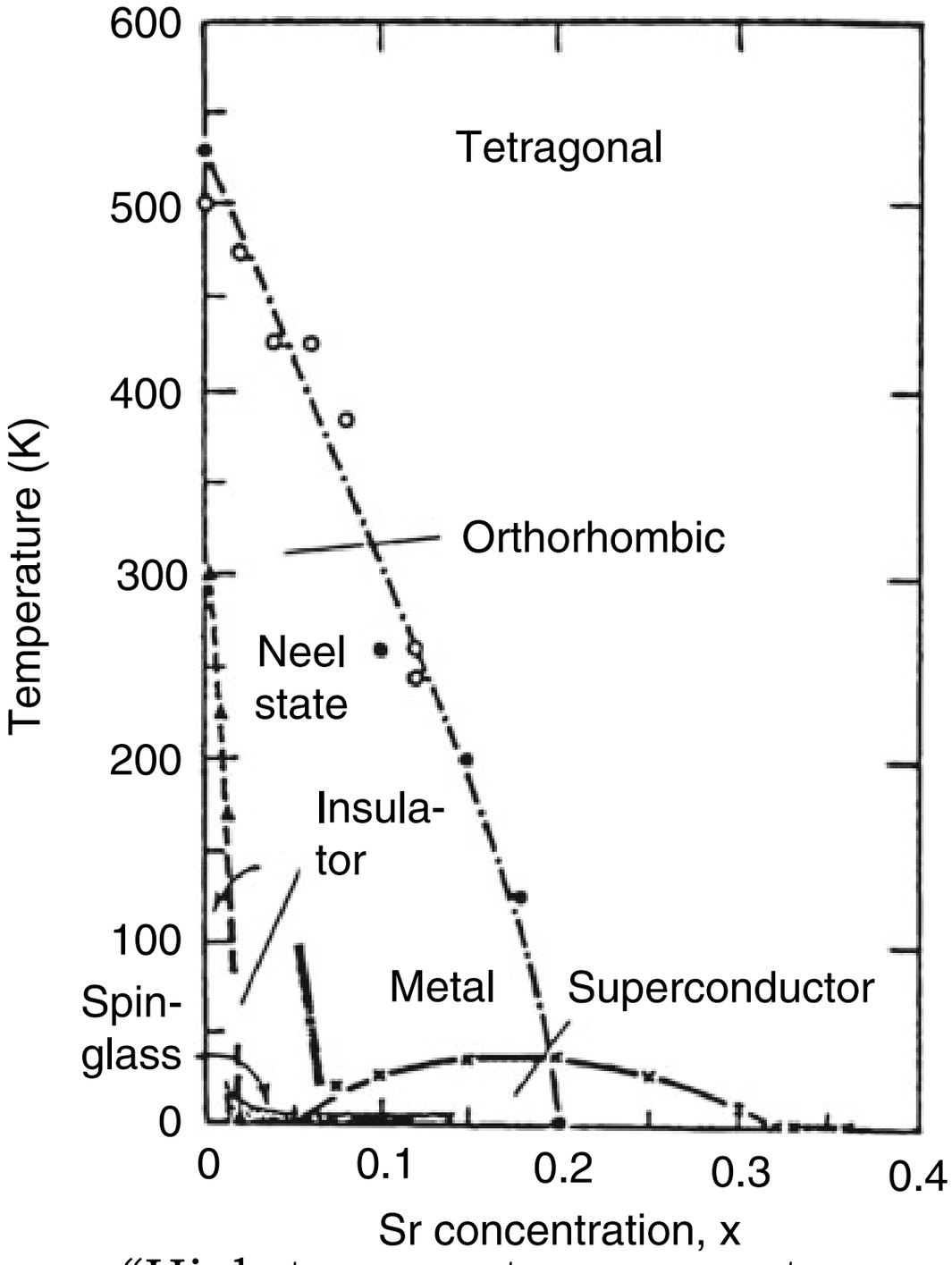
Non-conventional superconductivity

Superconductivity is emergent from interactions

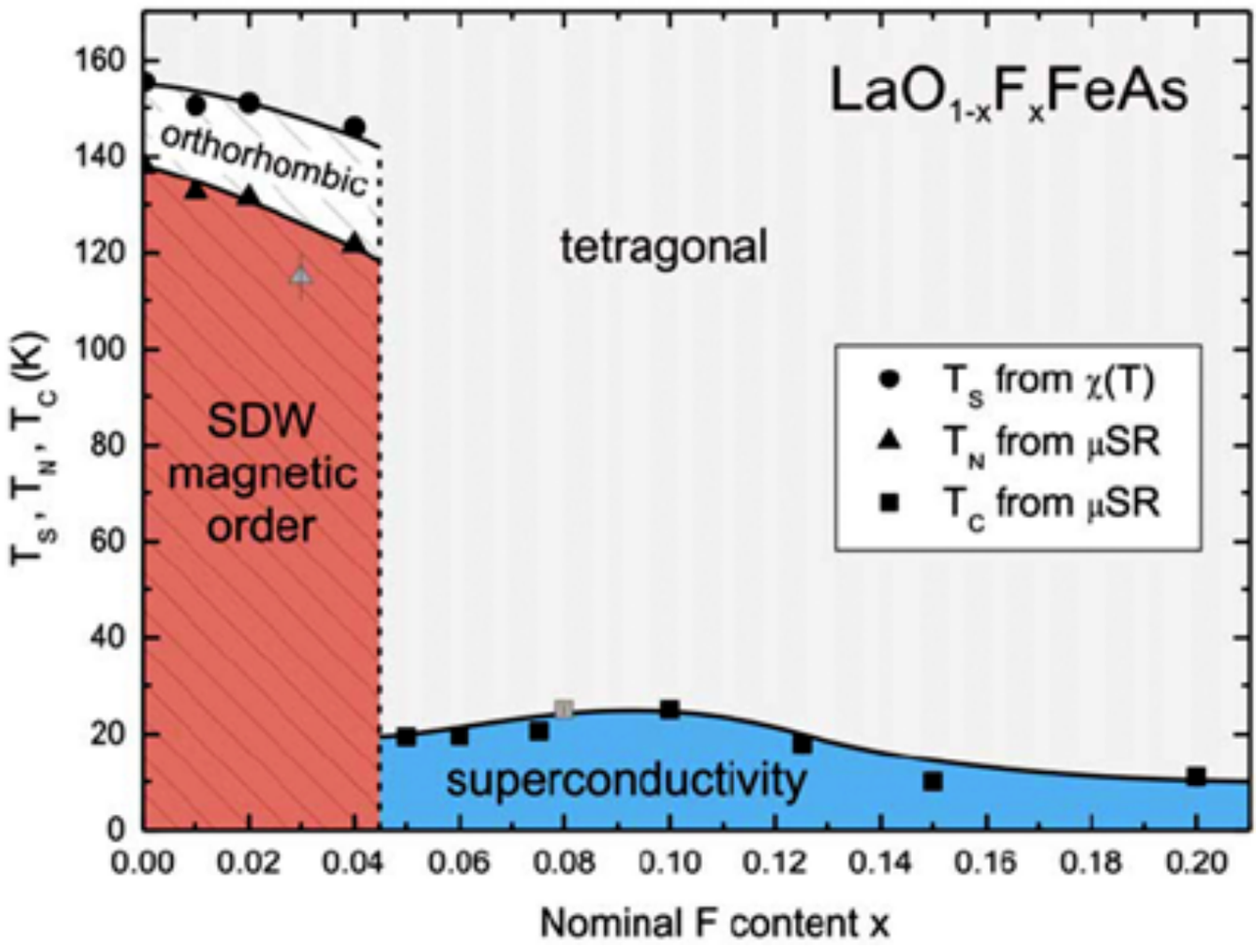
Most theoretical treatments: non-interacting system + some interaction.

None of these treatments is particularly satisfying.

Structure

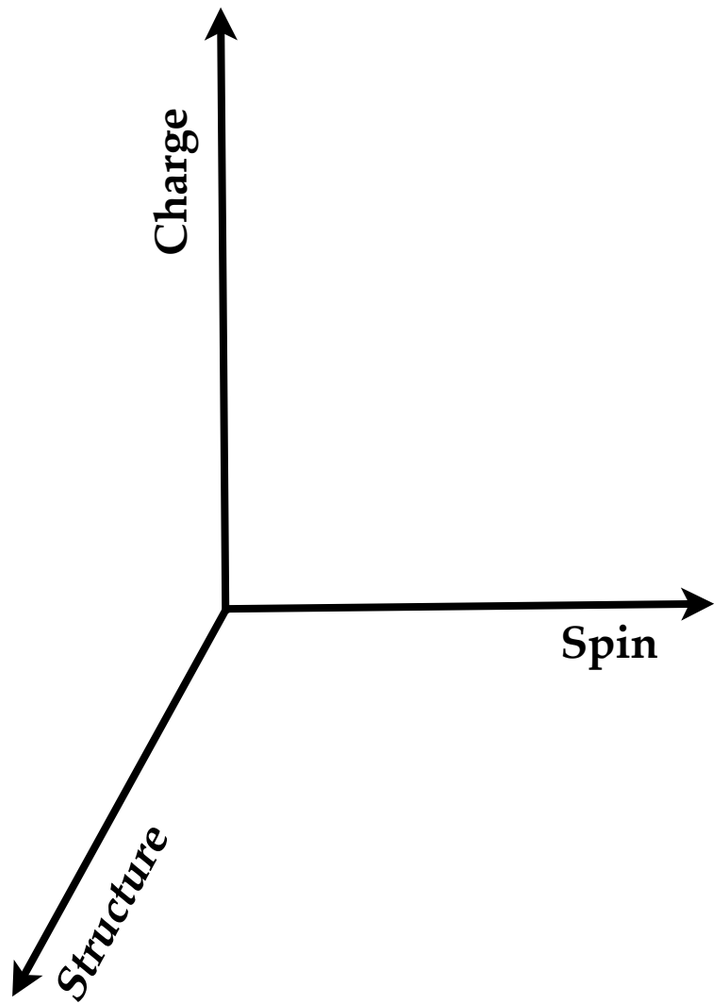


"High temperature cuprate superconductors" N. Plakida



Michael Norman
Physics **1**, 21 (2008)

Challenge of strongly correlated materials

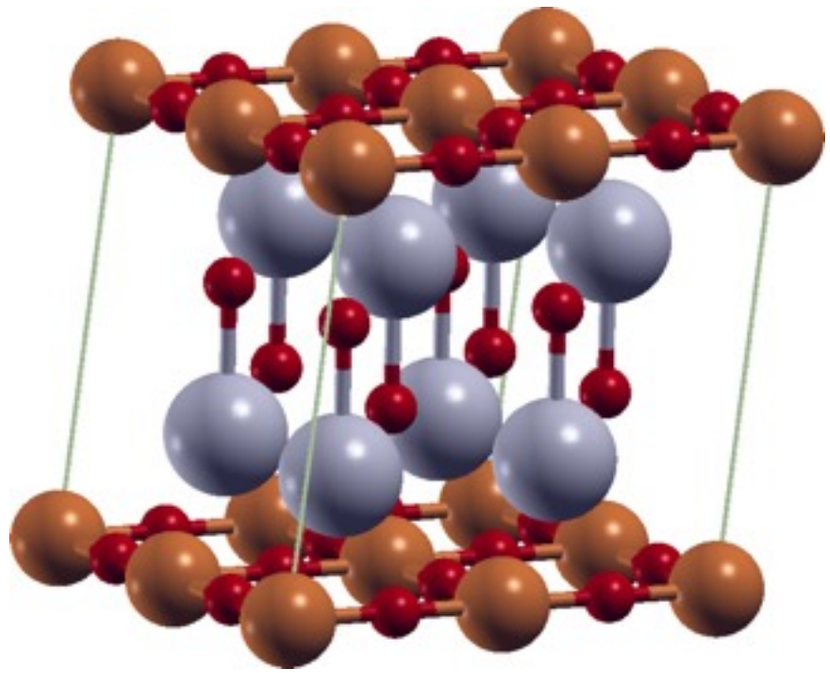


- 3 degrees of freedom in many materials
- up to 3-body interactions
- experiments usually probe only 1 degree of freedom
- opportunity for computation

Computational details

FN-DMC

Most are with small supercell
Checks for larger size cell

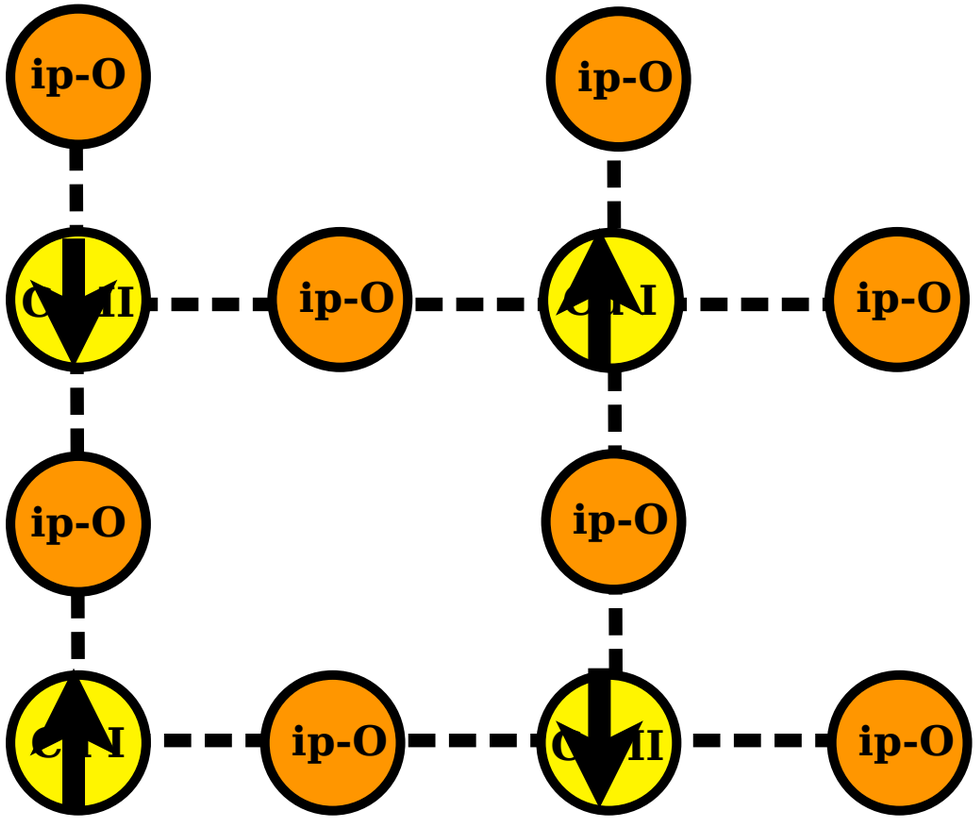


Twisted boundary conditions

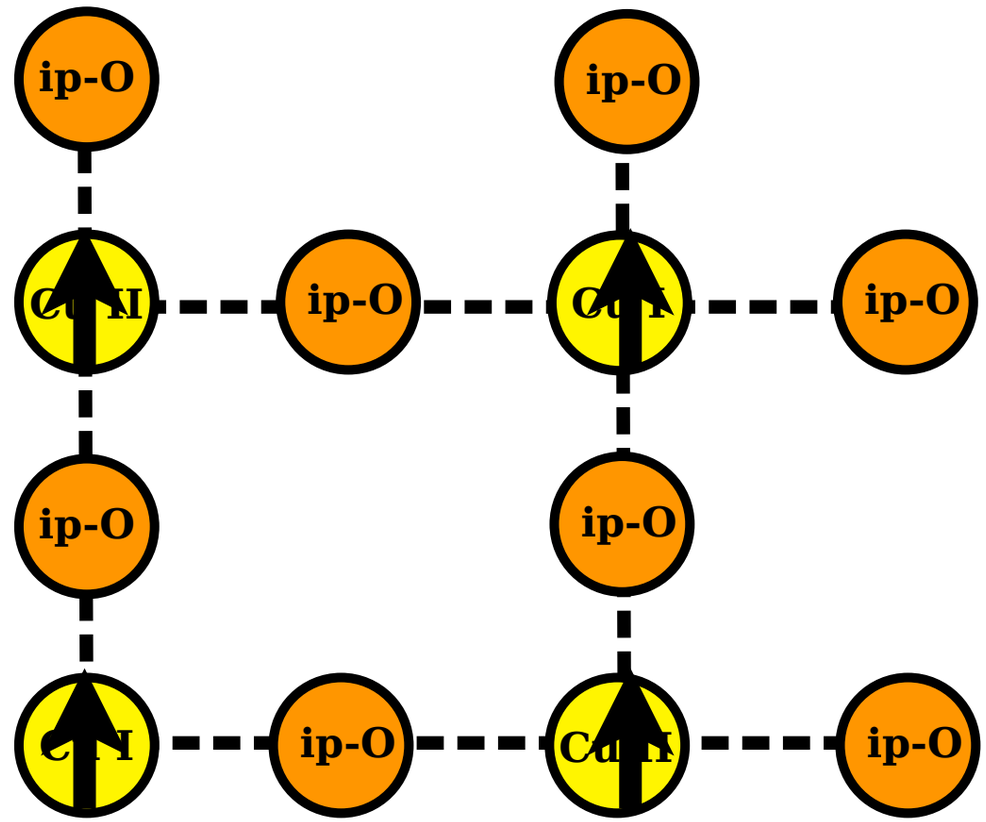
timestep=0.01 Hartrees^{-1}
PBE0 trial orbitals (semi-optimized)
CRYSTAL/QWalk

Explicit La substitution for 0.125 doping

Estimating J in cuprates



Spin anti-aligned (AFM)



Spin aligned (FM)

For Heisenberg model:

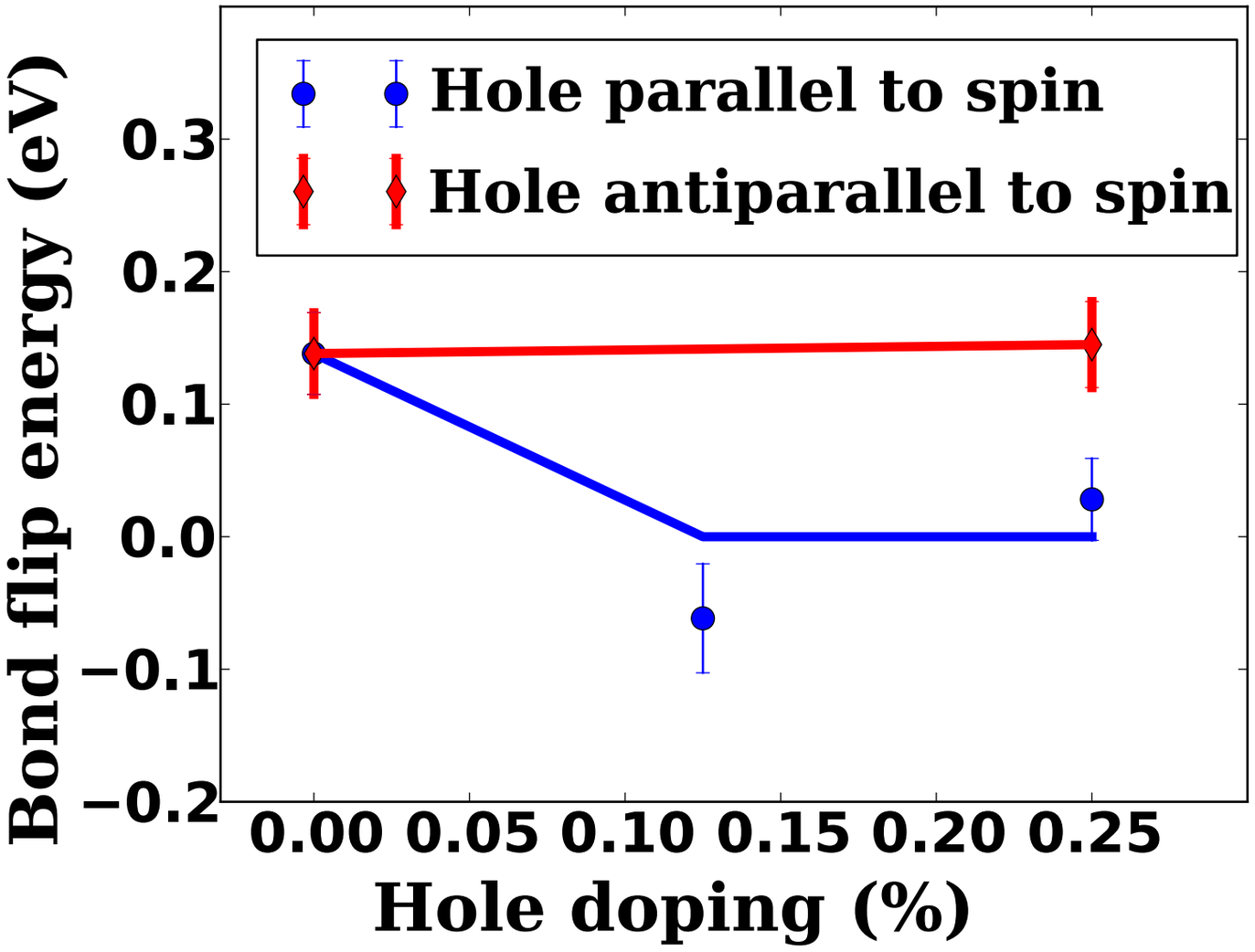
$$J \propto E(FM) - E(AFM)$$

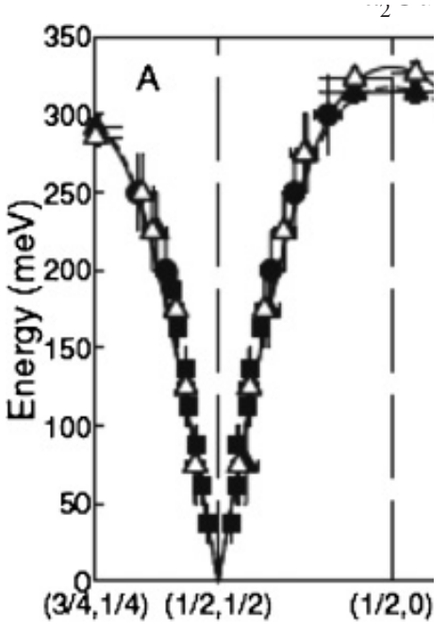
Numerical comparison to experiment

Quantity	FN-DMC	Experiment
J (eV)	0.14(3)	0.12
Magnetic moment of Cu (Bohr)	0.6	0.6
Quasiparticle gap (eV)	2.0(3)	2.2
B_{1g} phonon frequency (meV)	36(2)	40-42
A_{1g} phonon frequency (meV)	46(2)	>42

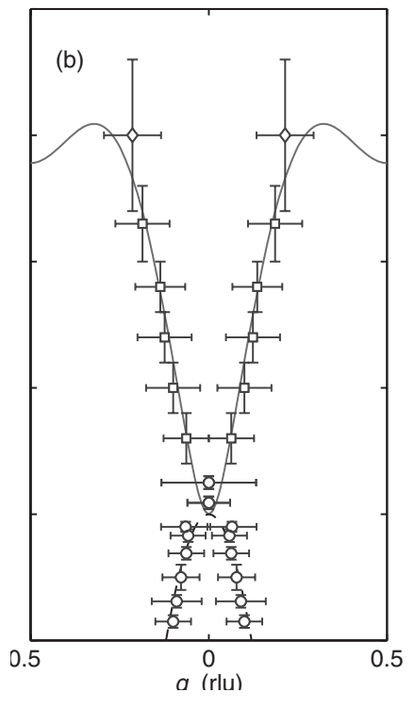
Very accurate results: no parameters!

Adding charges





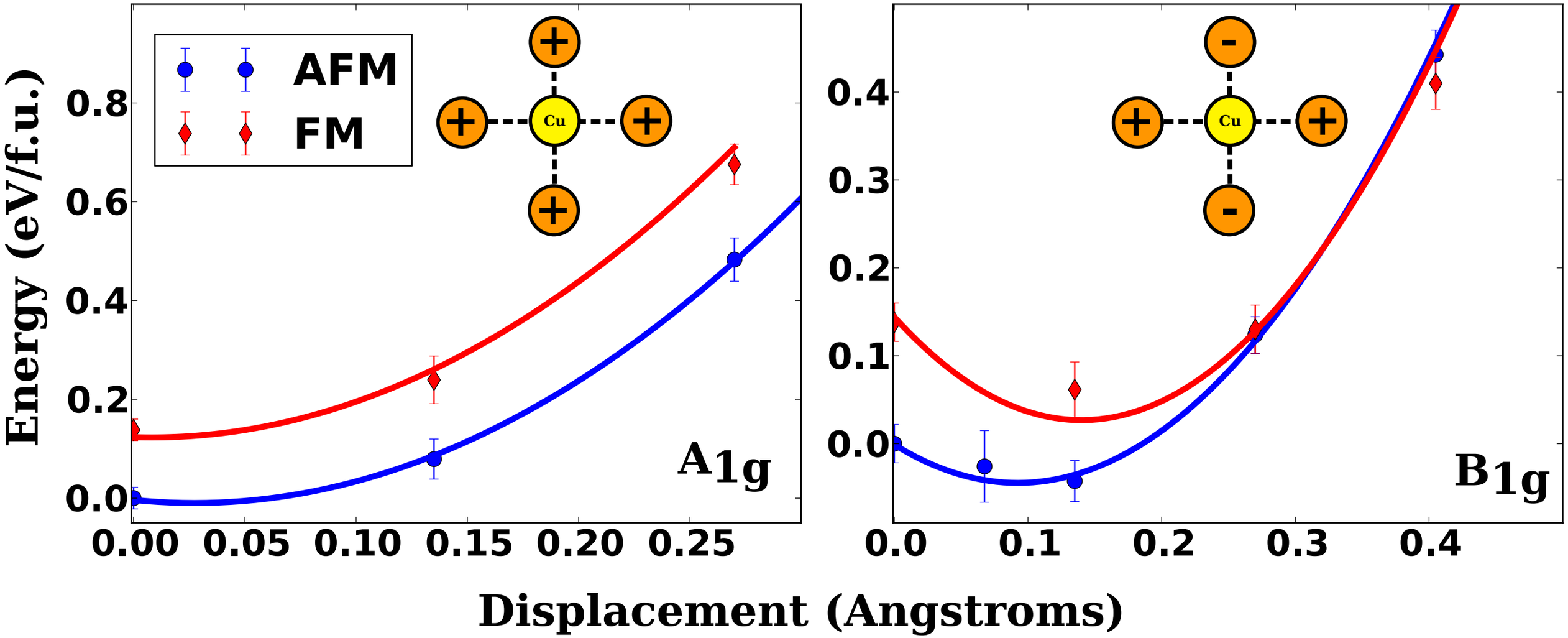
Undoped



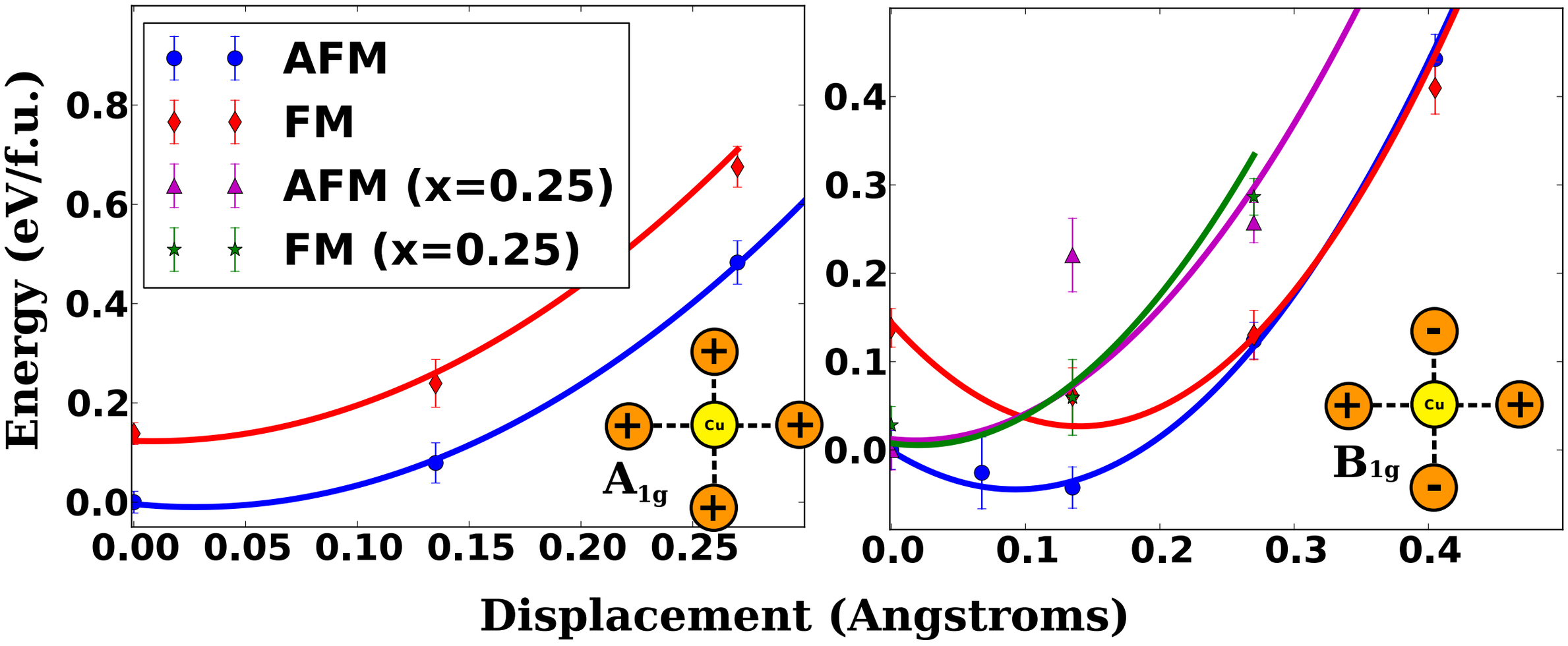
12.5%

Birgeneau et al. J. Phys. Soc. Jpn., Vol. 75, No. 11

Spin-lattice coupling

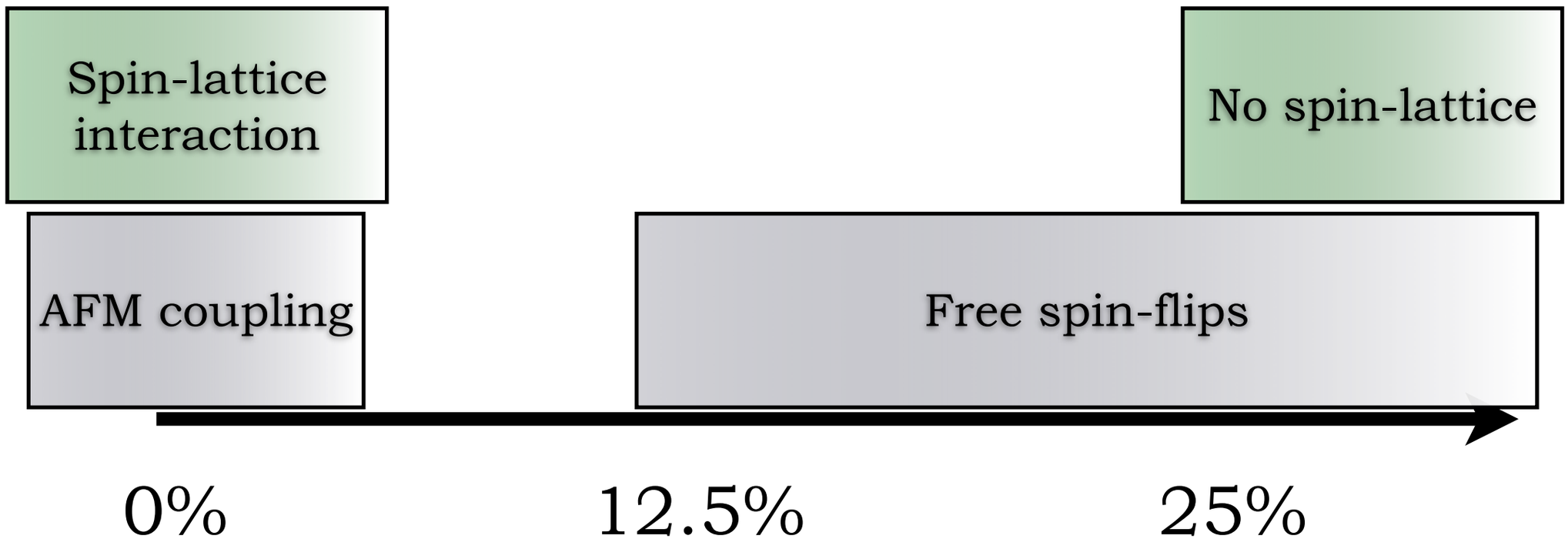


Some lattice degrees of freedom depend on the magnetic state strongly!



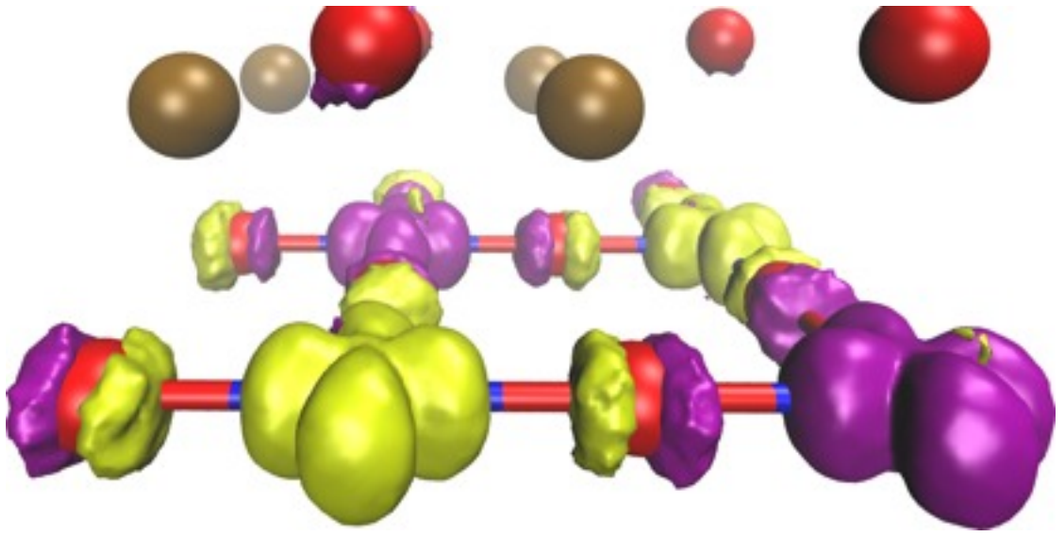
Spin-lattice coupling removed with 25% doping

Interactions

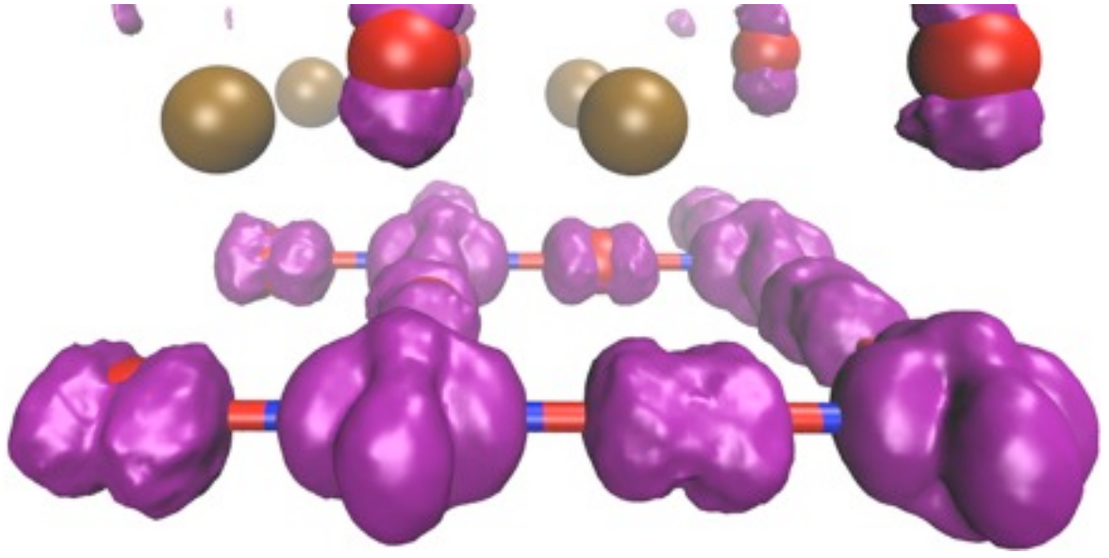


Origin of the strong spin coupling

AFM

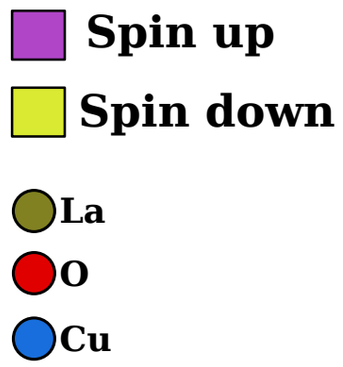


FM



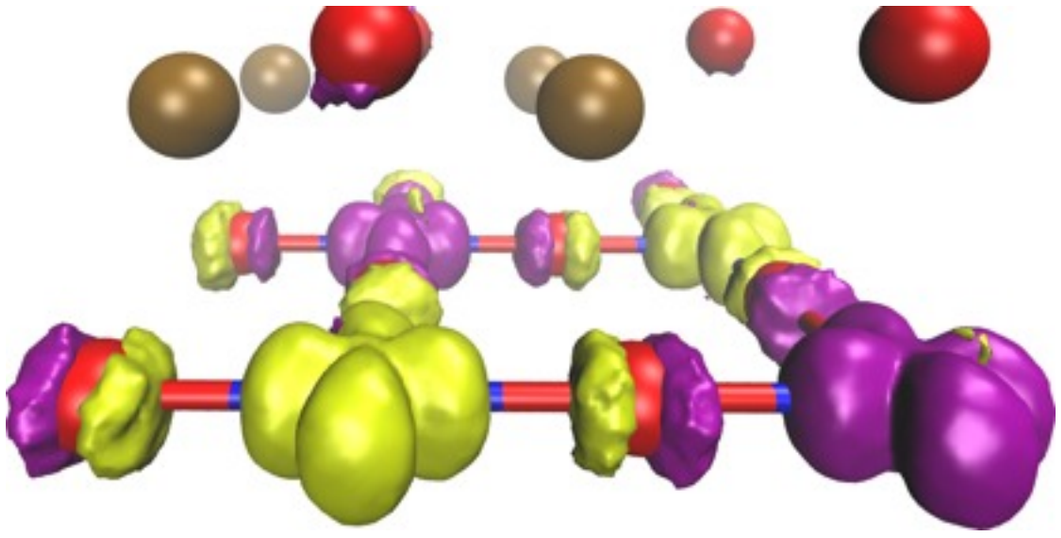
Overlap of spin density onto oxygen

d-p hybridization important!

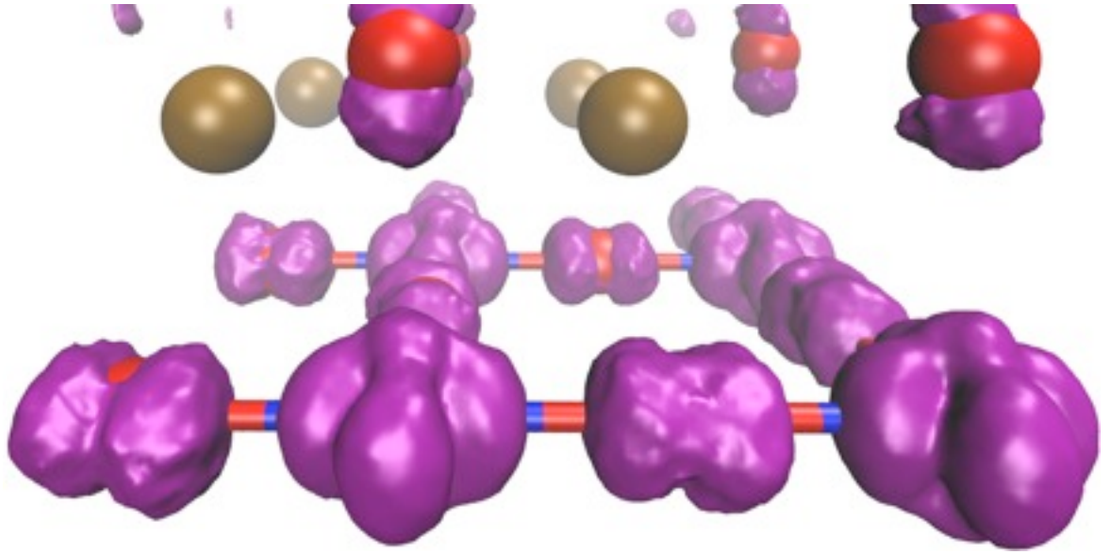


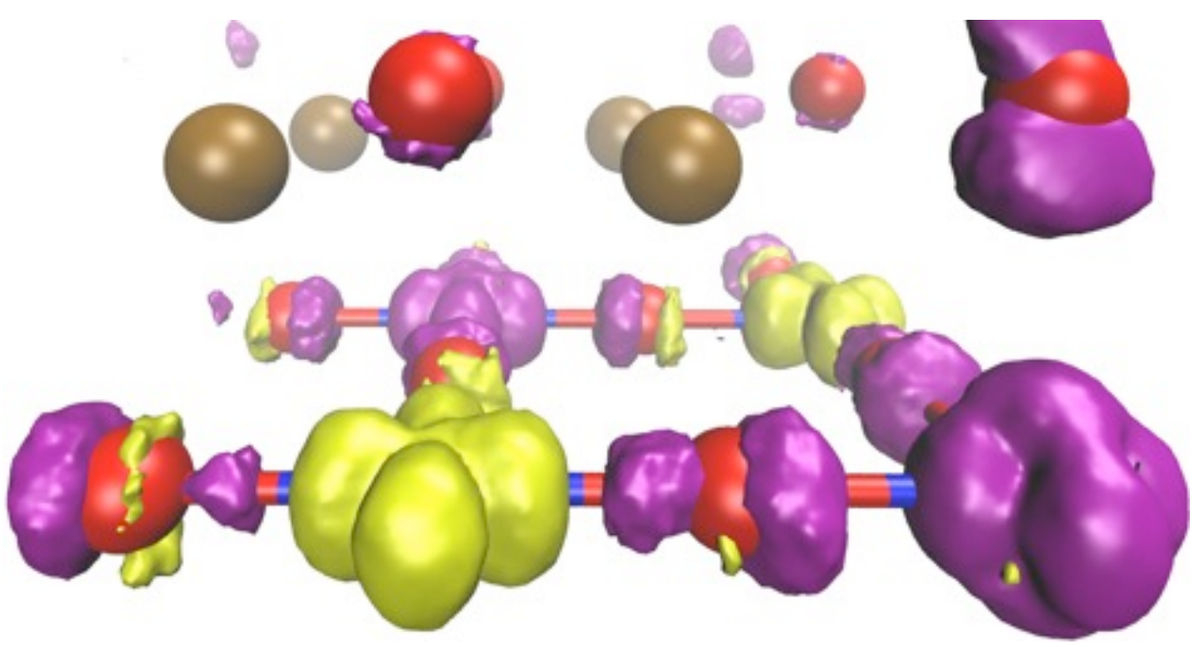
Why doping changes the spin spectrum

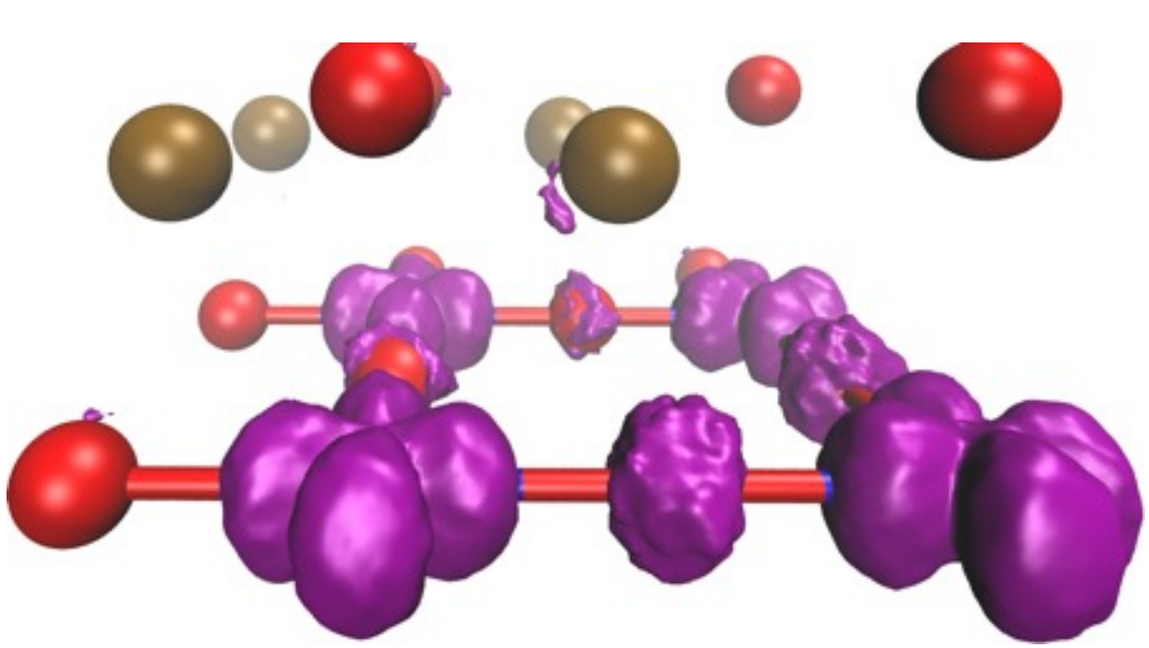
AFM



FM



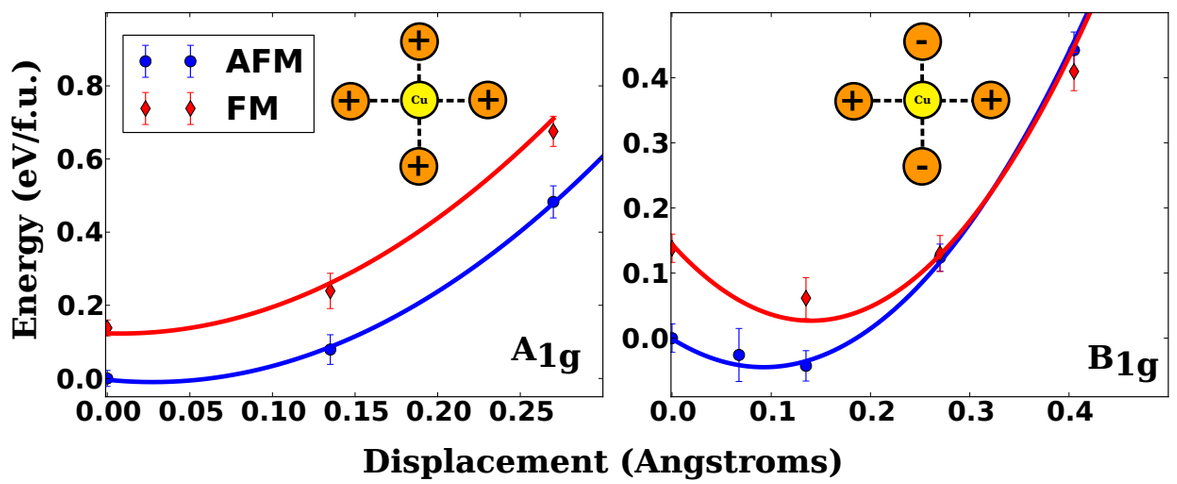


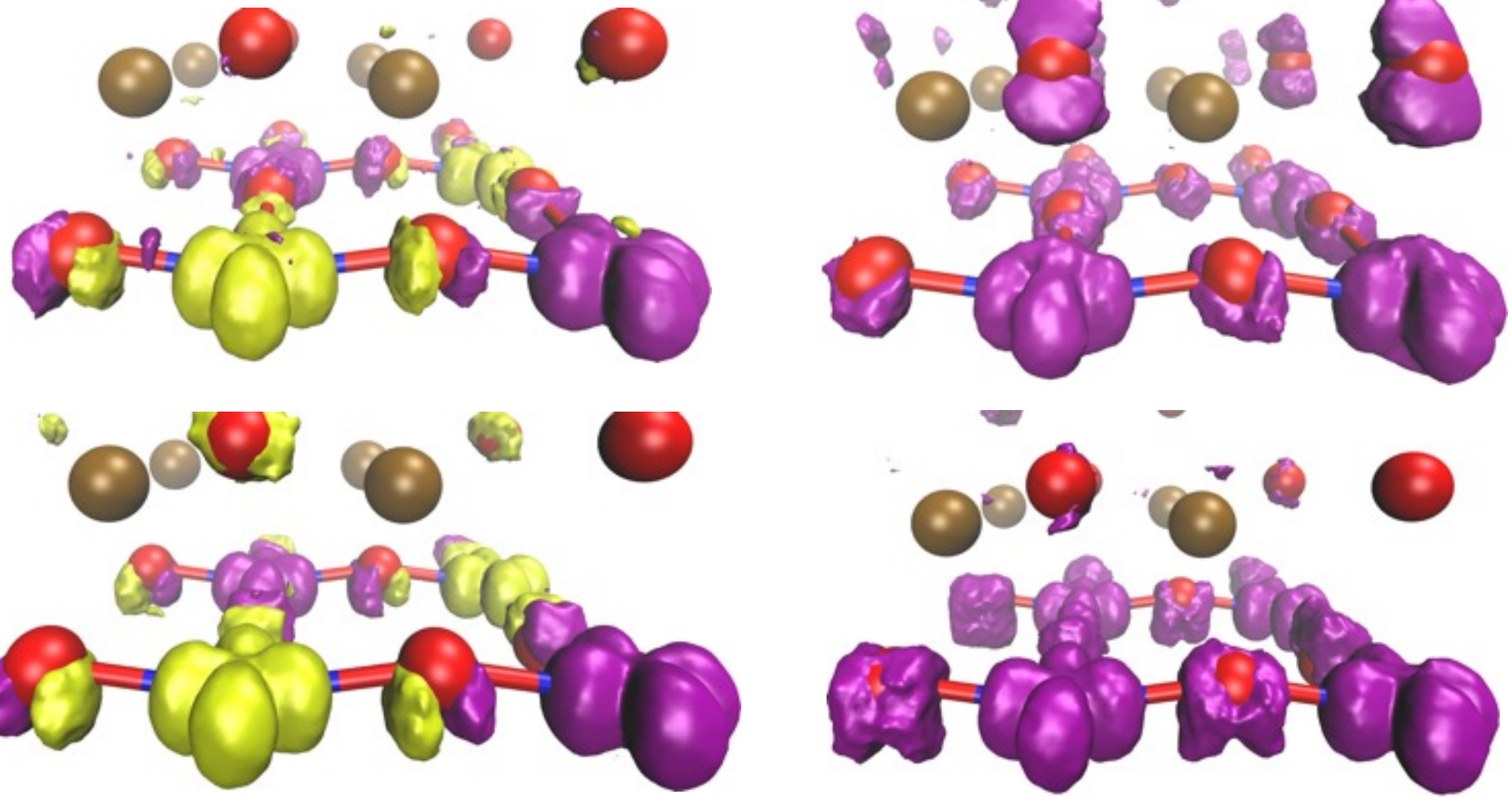


Hole sits mostly on the oxygen: removes spin coupling

The difference between the A1g and B1g

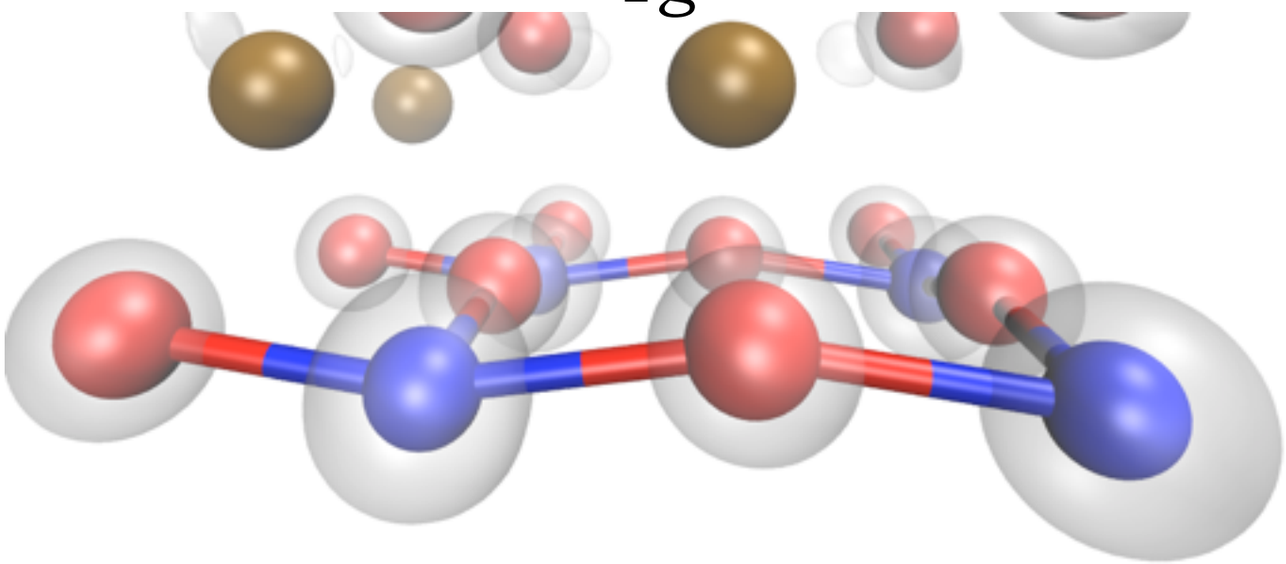
Difference is again on the oxygen atoms



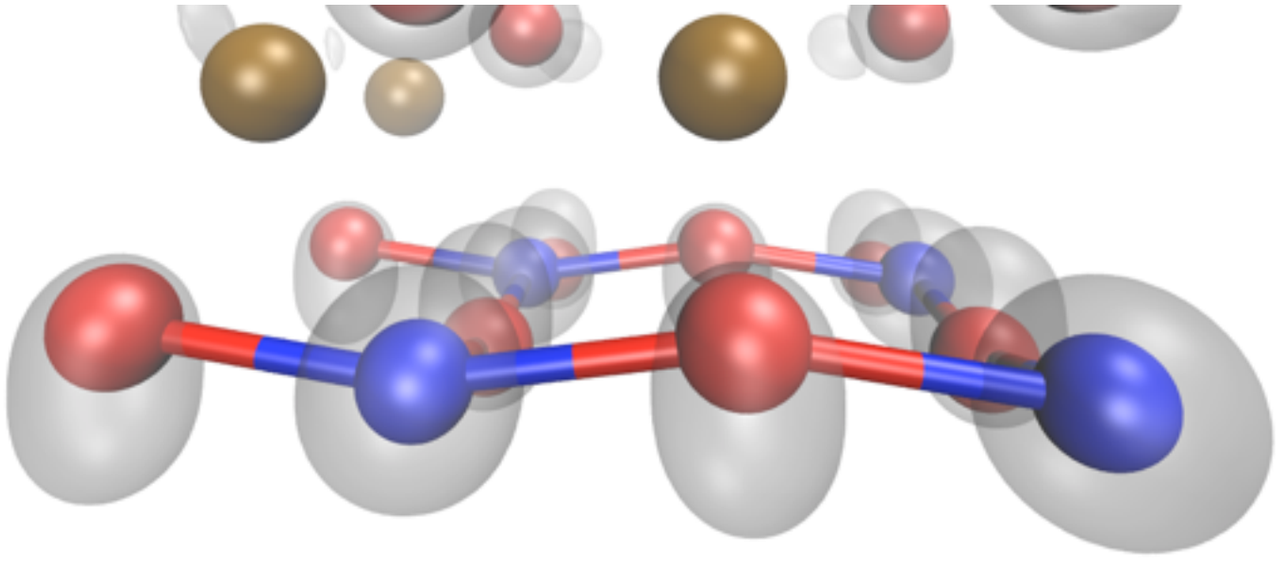


The charge density

A_{1g}



B_{1g}



B_{1g} mode has a dramatically different charge density

Summary

Correlation affects d-p hybridization

1-particle orbitals with good d-p hybridization->good FN-DMC results

In cuprates, d-p hybridization is cause of:

- strong AFM coupling
- spin-lattice coupling
- doping-dependence

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