Correlation in correlated materials (mostly transition metal oxides)

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- Understanding of correlated materials is mostly phenomenological

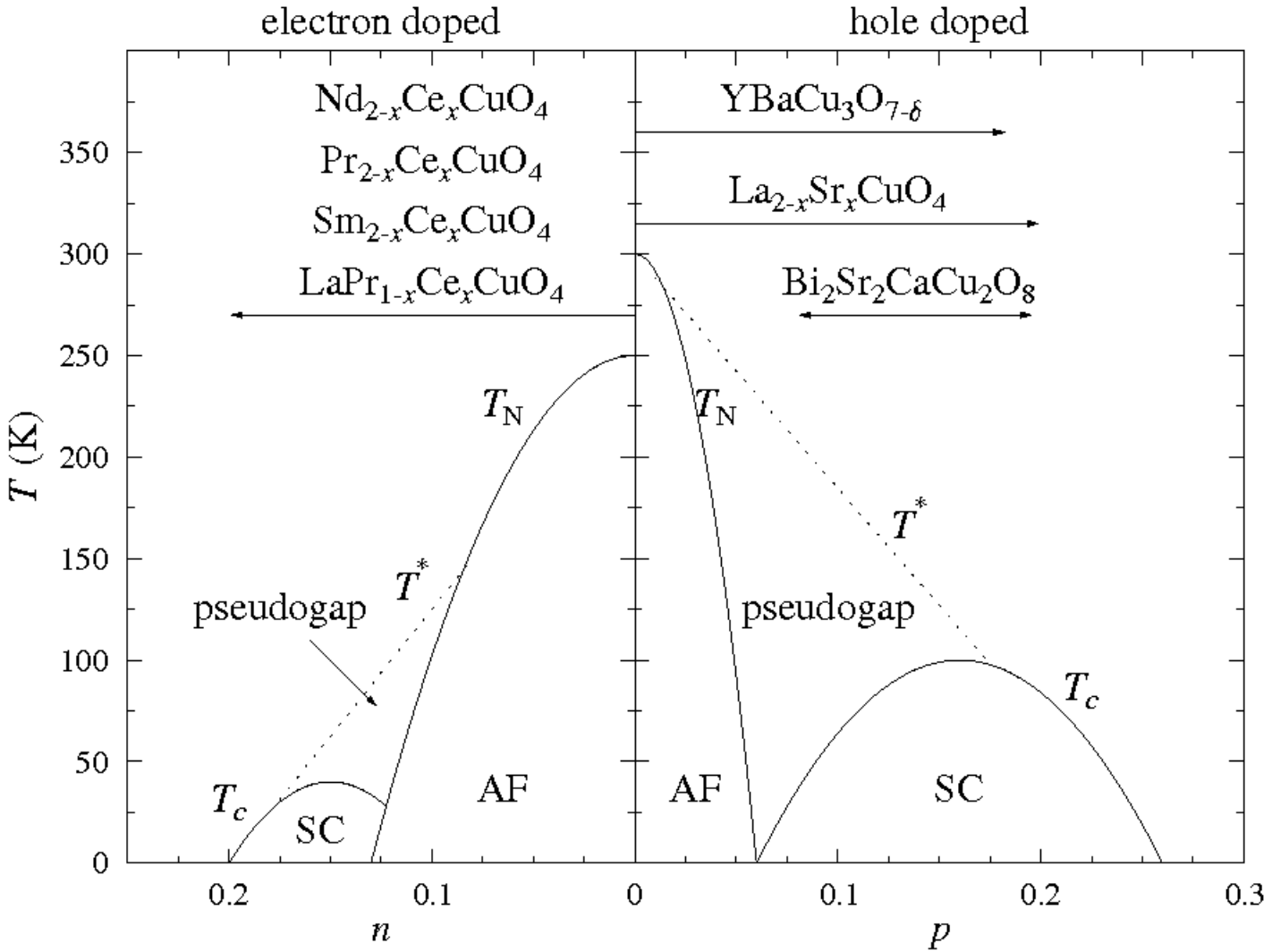
- FN-DMC (Slater-Jastrow): good energetics, but due to cancellation of errors

- Use reduced density matrices and accurate wave functions to calculate electron correlations

Transition metal oxides and attempts to describe them

Strongly correlated materials

High Tc superconductivity



After C. Hartinger

Phenomenological models of the physics:

- Hubbard model
- Valence bond theory

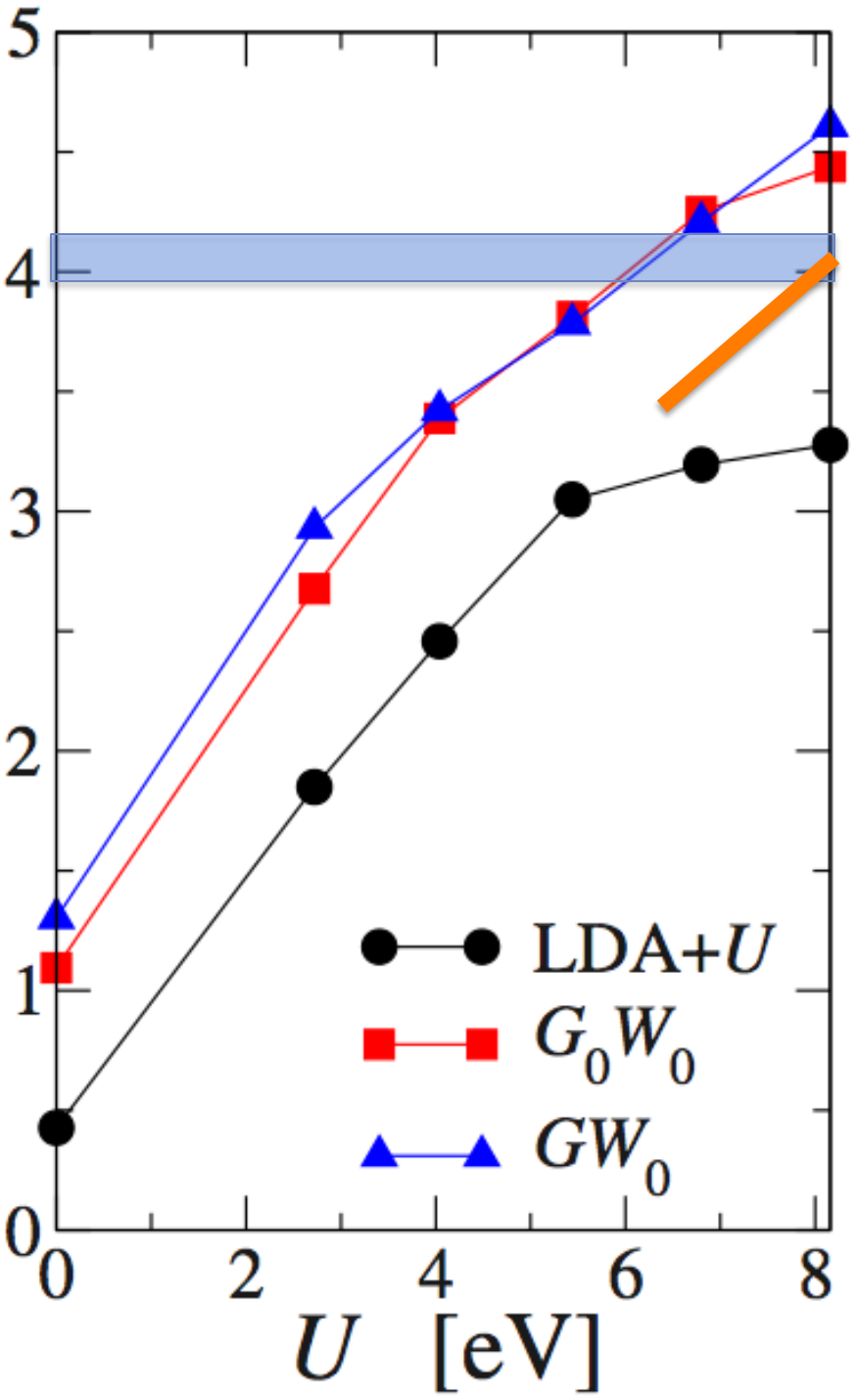
First principles calculations:

- DFT (hard to include correlation)
- Quantum chemistry (hard to apply to solids)
- Quantum Monte Carlo (fixed node?)
- GW (perturbation theory)

Phenomenological models + first principles:

- DFT+U
- DFT+DMFT

NiO: the band gap



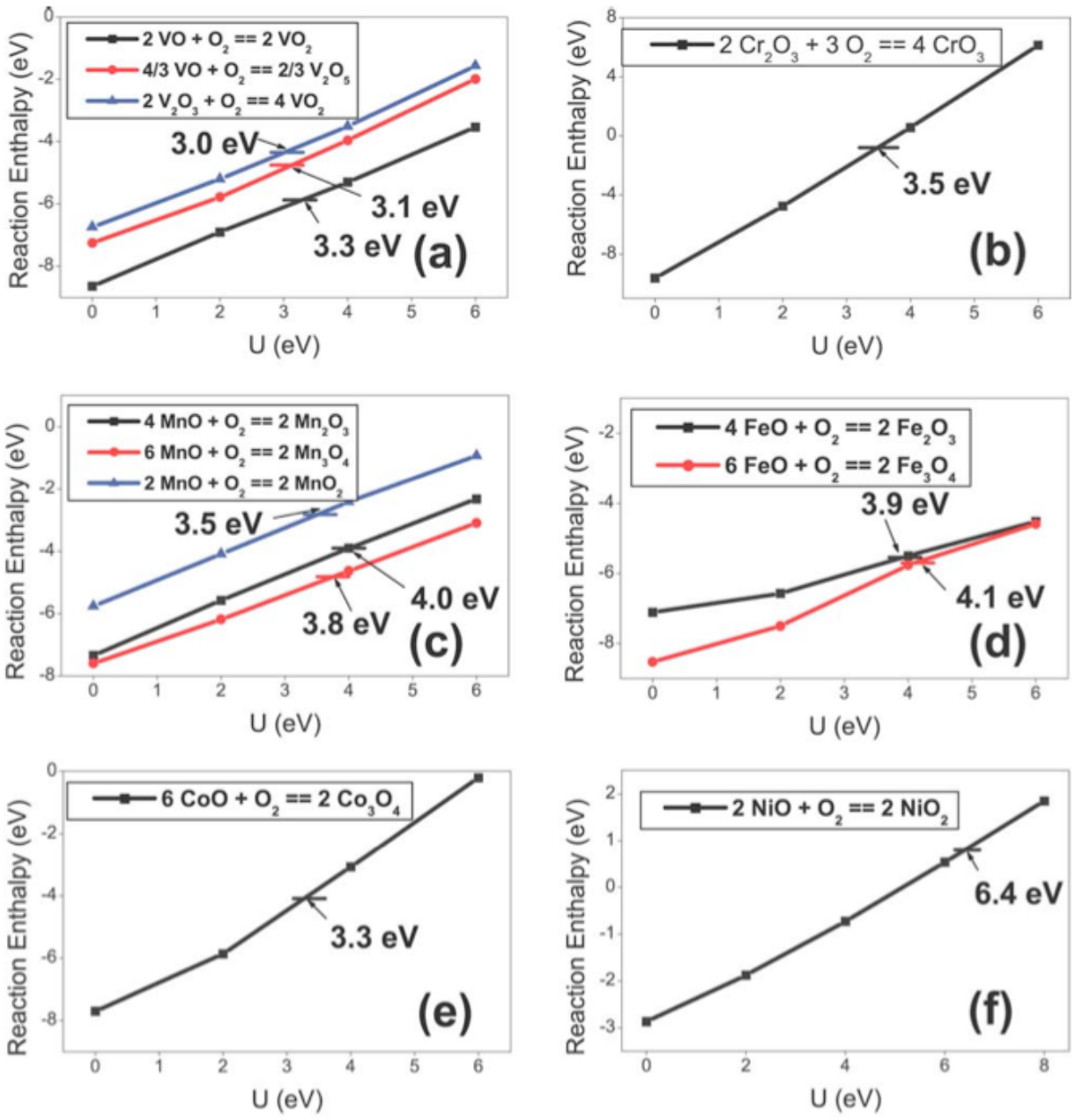
Experiment
LDA+DMFT

Jiang et al. PRB 82 045108 (2010)

Ren et al. PRB 74 195114 (2006)

Reaction enthalpies

U helps, but hard to use predictively



Wang, Maxisch, and Ceder. PRB **73,** 195107 (2006)

Problems with DFT+Hubbard:

Lots of (too much) flexibility:

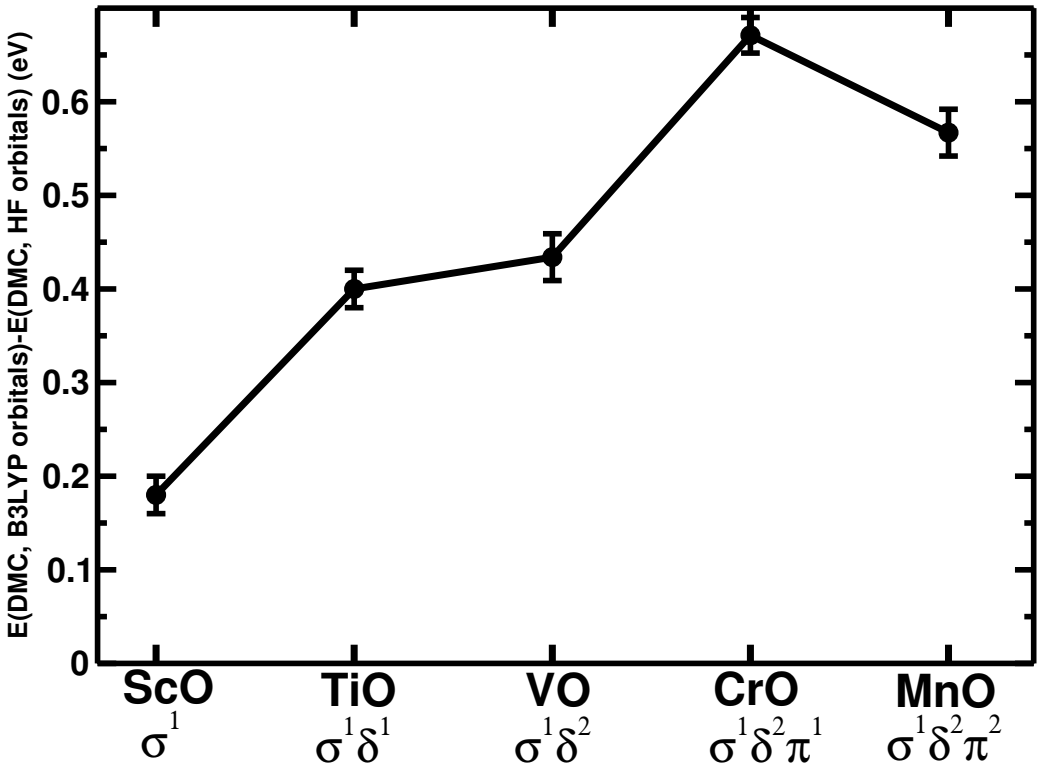
- Double-counting scheme
- Level of lattice model treatment
- Basis on which to apply lattice model
- How we choose the value of U
- Do we include intersite terms?

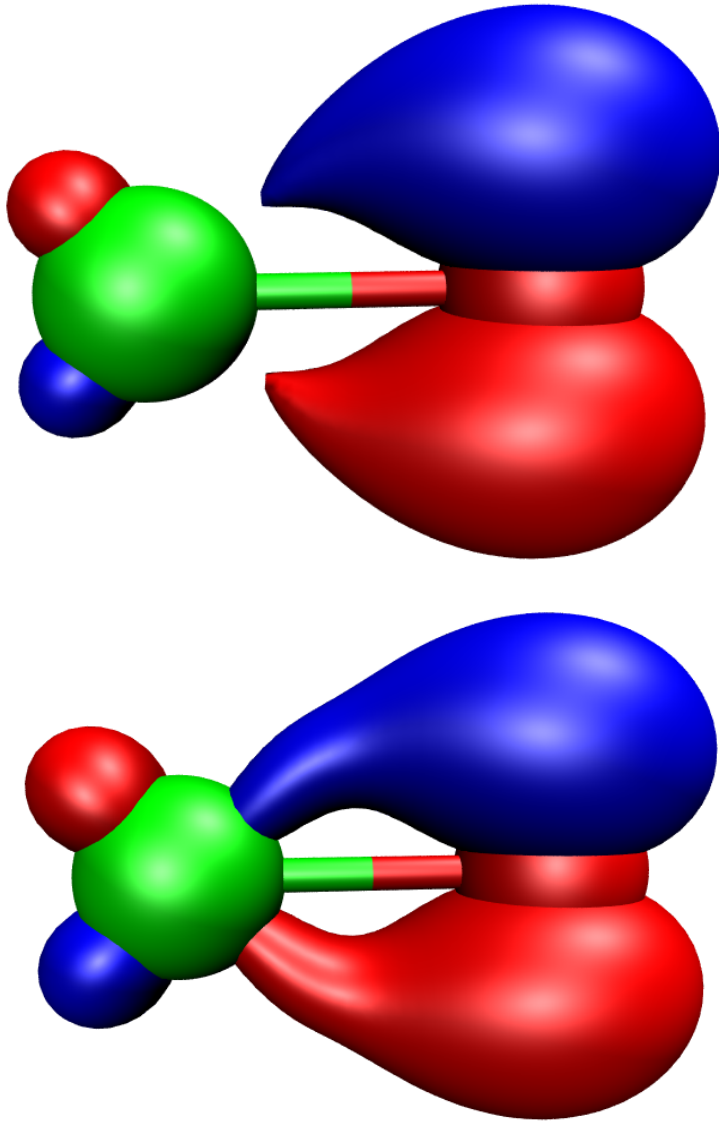
Little *a priori* guidance!

QMC methods to give guidance?

QMC calculations on transition metal oxide materials (a very brief summary)

Early work: TMO molecules





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

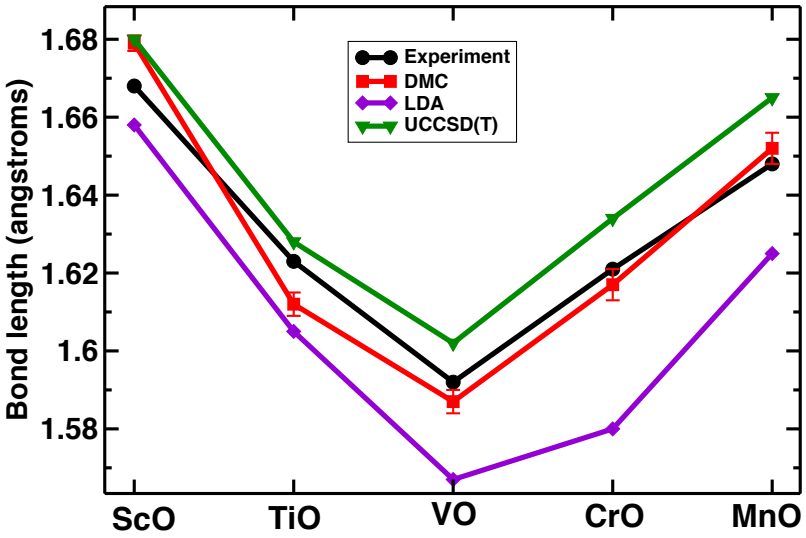
FN-DMC(SJ) energetics performance is pretty good

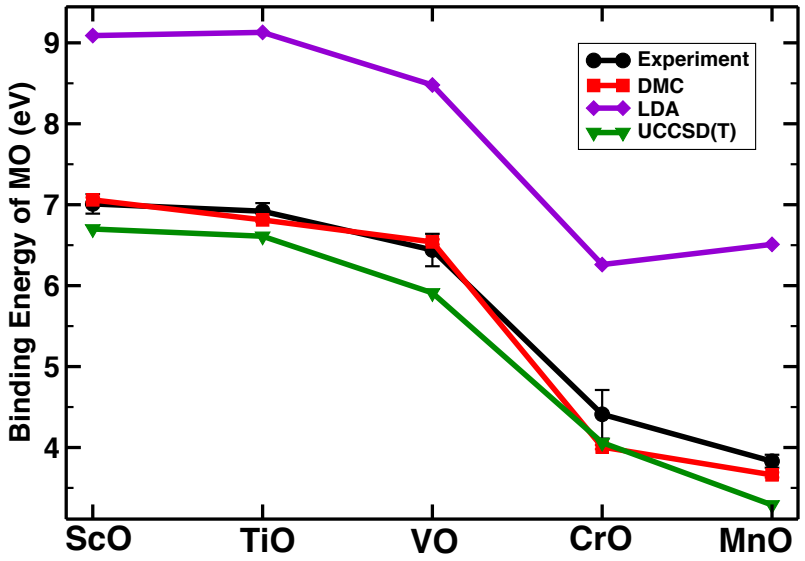
General note: d-p hybridization needs to be properly described for the best results. After that,

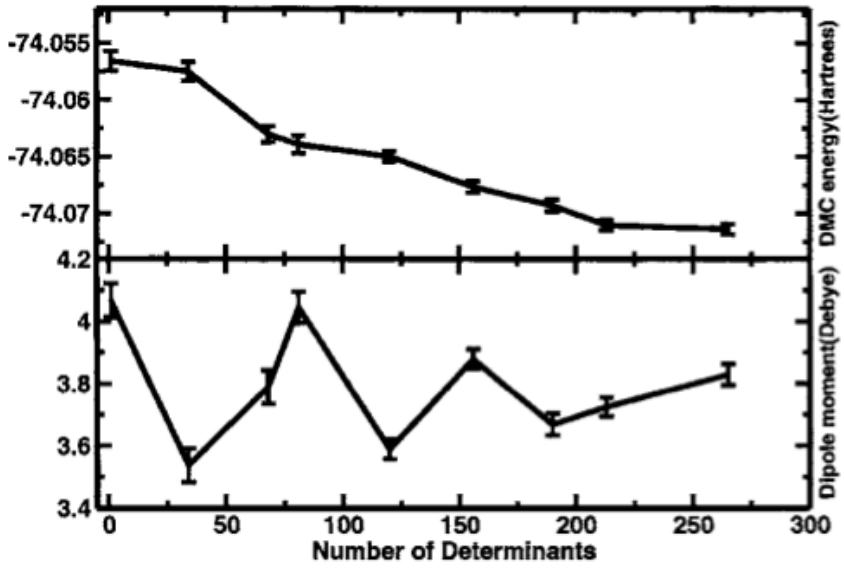
Cohesive energies in good agreement w/experiment:
MnO, **FeO**, **NiO**, **$BaTiO_3$**, **ZnO**, **V_xO_y**
Equations of state: FeO
Band Gap: FeO, MnO, $BaTiO_3$, ZnO

- Needs and Towler Int. J. Mod. Phys. B. 17 5425 (2003)
- Wagner, J. Phys.: Condens. Matter 19 343201 (2007)
- Kolorenc and Mitas, Phys. Rev. Lett. 101, 185502 (2008)
- Kolorenc, Hu, and Mitas, Phys. Rev. B 82, 115108 (2010)
- Ertekin, Wagner, and Grossman, (in preparation)
- Bande and Luchow, Phys. Chem. Chem. Phys., 2008, 10, 3371

Signs of trouble: TMO molecules







Bond length and binding energy are very close to experiment when using B3LYP orbitals

But the dipole moment still changes a lot with multiple determinants!

Despite encouraging energetic performance, there are indications that the wave function is not very good at the DMC(SJ) level!

Going forward

- **Guess wave functions**
  (hope they work)
- **General wave function expansion**
  (but the space is exponential!)
- **Understand the physics**
  (too hard?)

Analyzing electron correlation using reduced density matrices

Understand the physics

This has two purposes:

- Get better accuracy in QMC
- Help understand the physics of TMO materials

Strong correlations?

Physicists: Strong electron-electron term in effective low-energy Hamiltonian (Hubbard U)

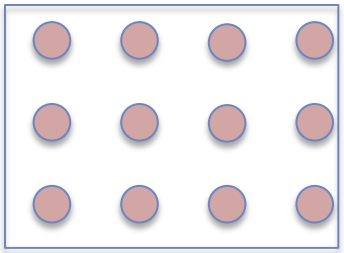
Chemists: Large “static” correlation (left-right correlation)

Electron in place A → another electron not in place A

Correlation in electron gas

$$\hat{H} = -\frac{1}{2}\sum_i \nabla_i^2 + \sum_{i<j} \frac{1}{r_{ij}}$$

High density: kinetic energy dominates



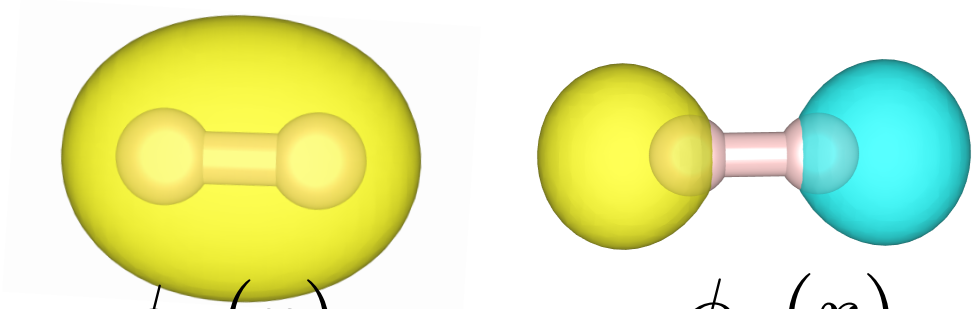
Low density: Coulomb energy dominates

Left-right correlation: H_2 molecule

Electron-nucleus and kinetic energy dominate

Electron-nucleus smaller, kinetic energy smaller:
Electron on A → other electron on B

Introduction to density matrices



$\phi_1(r)$ $\phi_2(r)$

Ansatz:

$$\Psi(r_1, r_2) = a_1\phi_1(r_1)\phi_1(r_2) - a_2\phi_2(r_1)\phi_2(r_2)$$

$$\Psi(r_1, r_2) = a_1\phi_1(r_1)\phi_1(r_2) - a_2\phi_2(r_1)\phi_2(r_2)$$

$$\rho_{ij}^{1RDM} = \langle\Psi|c_i^\dagger c_j|\Psi\rangle$$

$$\rho^{1RDM} = \begin{pmatrix} a_1^2 & 0 \\ 0 & a_2^2 \end{pmatrix}$$

$$\rho_{ij,ij}^{2RDM} = \langle\Psi|c_i^\dagger c_j^\dagger c_i c_j|\Psi\rangle$$

$$\rho_d^{2RDM} = \begin{pmatrix} a_1^2 & 0 \\ 0 & a_2^2 \end{pmatrix}$$

$$\rho_{ij}^c = \rho_{ij,ij}^{2RDM} - \rho_{ii}^{1RDM}\rho_{jj}^{1RDM}$$

$$\rho^c = \begin{pmatrix} a_1^2 - a_1^4 & -a_1^2 a_2^2 \\ -a_1^2 a_2^2 & a_2^2 - a_2^4 \end{pmatrix}$$

General case

$$\rho^{1RDM} = \begin{pmatrix} a_1^2 & 0 \\ 0 & a_2^2 \end{pmatrix}$$

$$\rho_d^{2RDM} = \begin{pmatrix} a_1^2 & 0 \\ 0 & a_2^2 \end{pmatrix}$$

$$\rho^c = \begin{pmatrix} a_1^2 - a_1^4 & -a_1^2 a_2^2 \\ -a_1^2 a_2^2 & a_2^2 - a_2^4 \end{pmatrix}$$

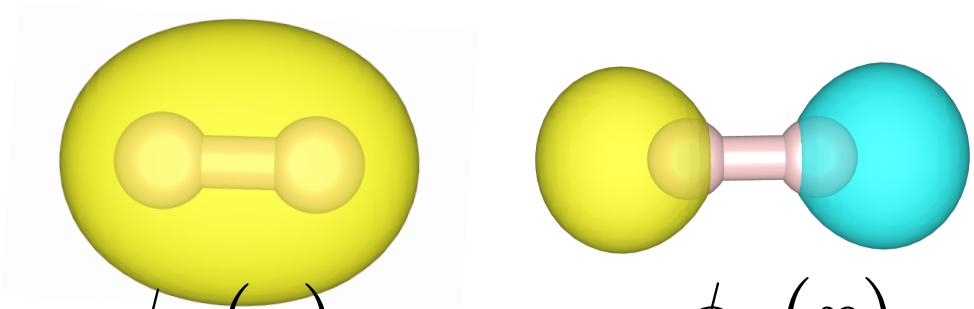
$$\Psi(r_1, r_2) = \phi_1(r_1)\phi_1(r_1)$$

$$\rho^{1RDM} = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}$$

$$\rho_d^{2RDM} = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}$$

$$\rho^c = \begin{pmatrix} 0 & 0 \\ 0 & 0 \end{pmatrix}$$

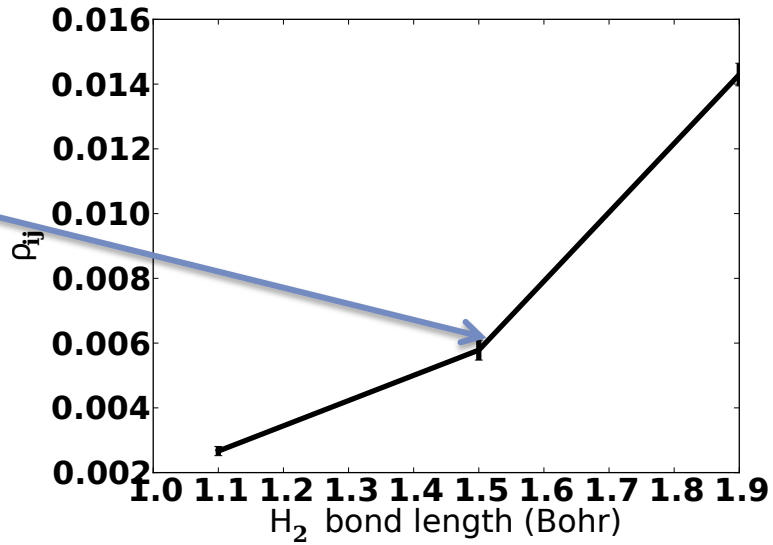
2-RDM diagonal



$\phi_1(r)$ $\phi_2(r)$

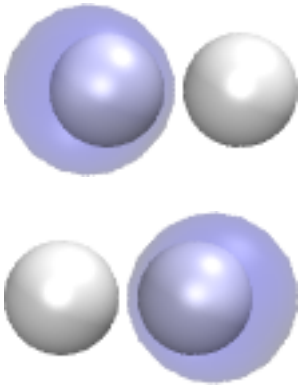
$$\Psi(r_1, r_2) \simeq \phi_1(r_1)\phi_1(r_2) - c\phi_2(r_1)\phi_2(r_2)$$

$$\rho_d^{2RDM} = \begin{pmatrix} a_1^2 & 0 \\ 0 & a_2^2 \end{pmatrix}$$

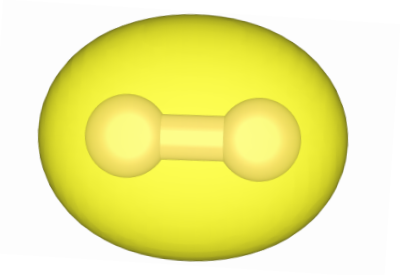


Relation to Hubbard picture

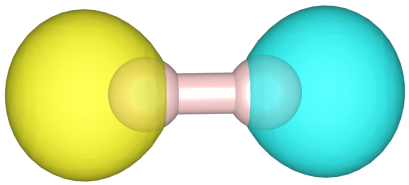
If we change basis:

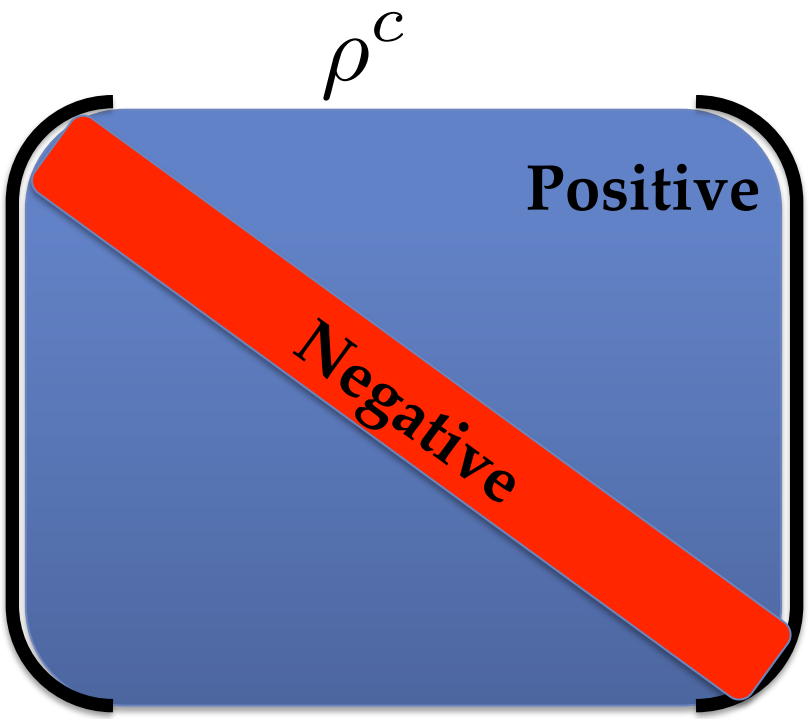


$$\rho^c = \frac{1}{2}\begin{pmatrix} -a_1 a_2 & a_1 a_2 \\ a_1 a_2 & -a_1 a_2 \end{pmatrix}$$

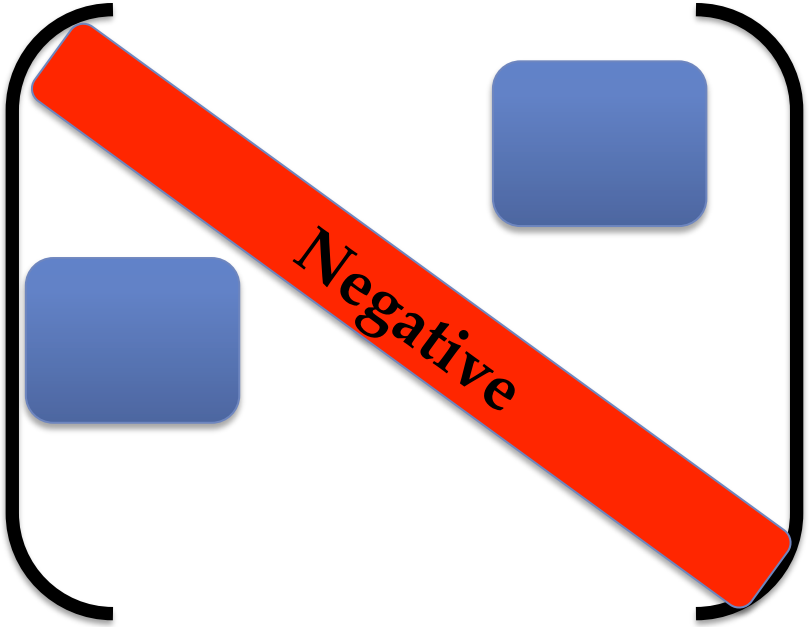


$$\rho^c = \begin{pmatrix} a_1^2 - a_1^4 & -a_1^2 a_2^2 \\ -a_1^2 a_2^2 & a_2^2 - a_2^4 \end{pmatrix}$$





Only on-site repulsion:



More complex structure:

$$\rho^c = \begin{pmatrix} a_1^2 - a_1^4 & -a_1^2 a_2^2 \\ -a_1^2 a_2^2 & a_2^2 - a_2^4 \end{pmatrix}$$

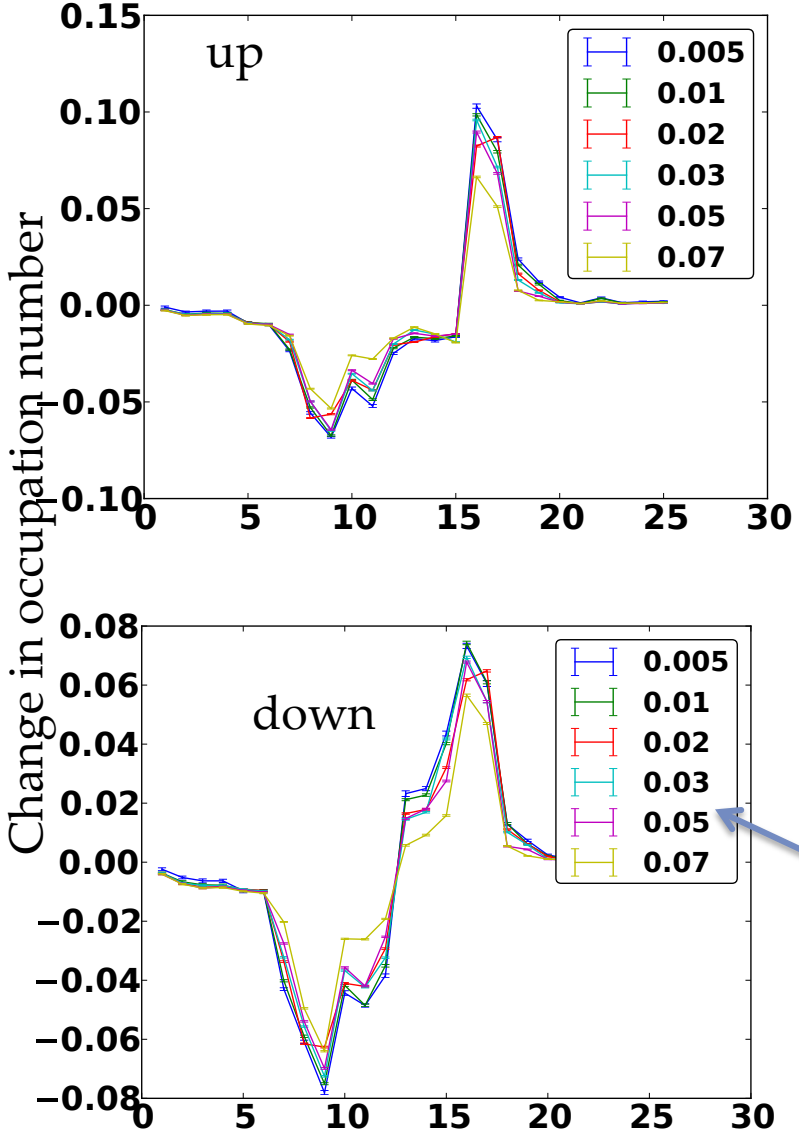
Most sets of four orbitals give rise to real-space repulsion with this pattern
Including combinations of localized and diffuse orbitals.

$$\rho^c = \frac{1}{2} \begin{pmatrix} -a_1 a_2 & a_1 a_2 \\ a_1 a_2 & -a_1 a_2 \end{pmatrix}$$

Localized sets of orbitals give this pattern

Evaluating electron correlation in transition metal oxides

MnO_2 convergence



ScO

TiO

VO

CrO

MnO **MnO_2**

FeO_2

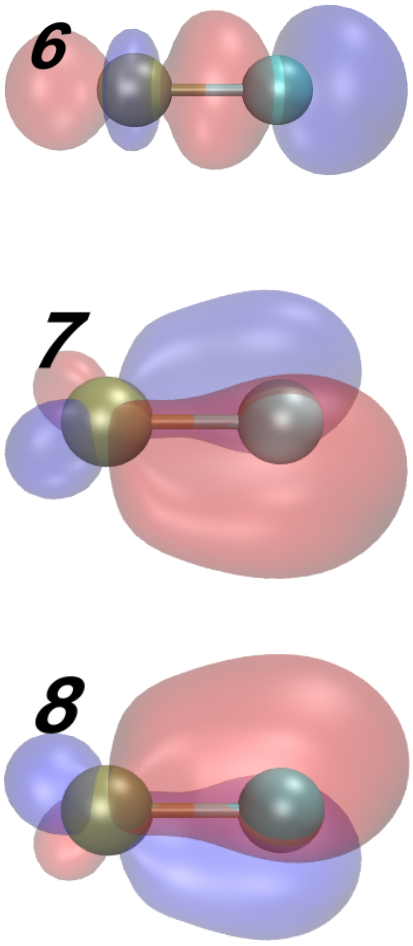
CoO_2

- Use small molecules
- Expand in Slater determinants, only doubles
- Converge the 1-RDM of the wave function with respect to determinants

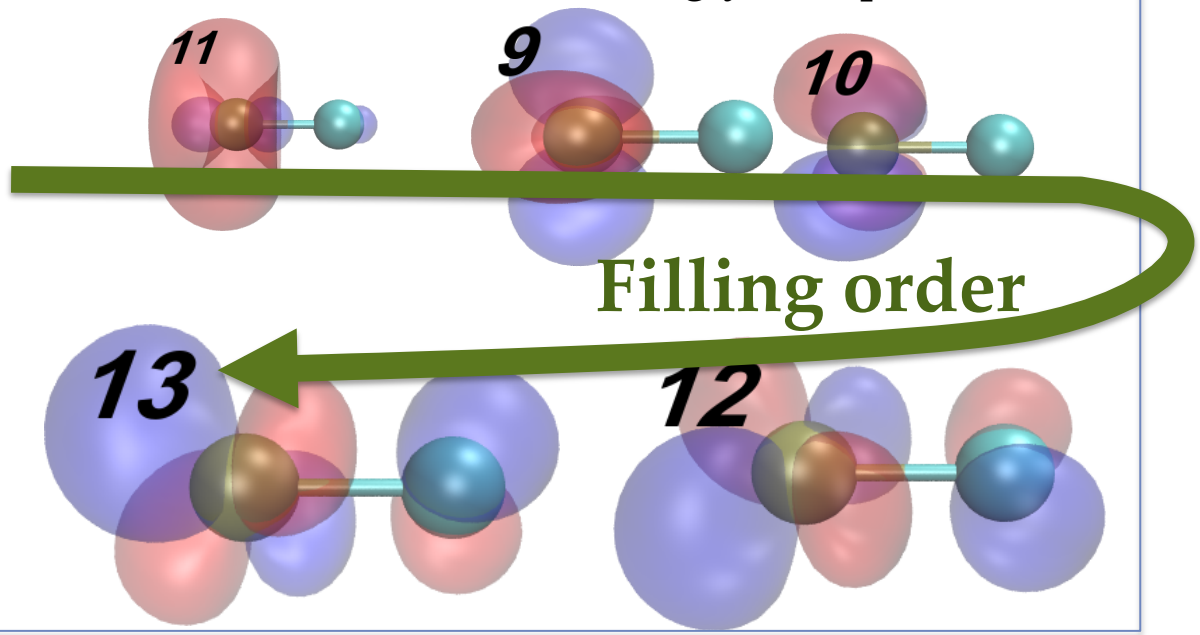
Cutoff threshold

Electronic structure of the TM monoxides

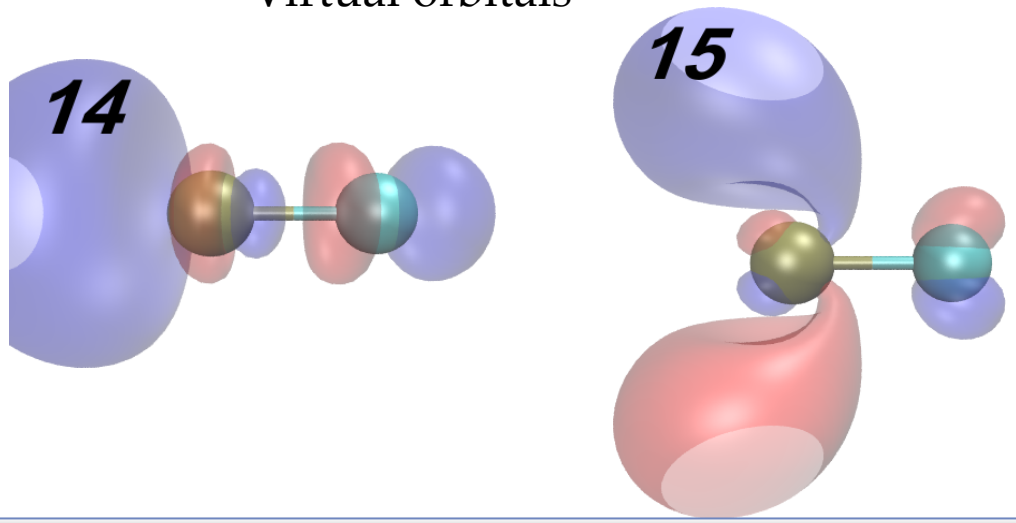
Doubly occupied



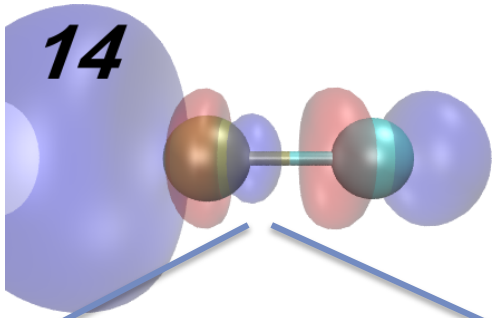
Singly occupied

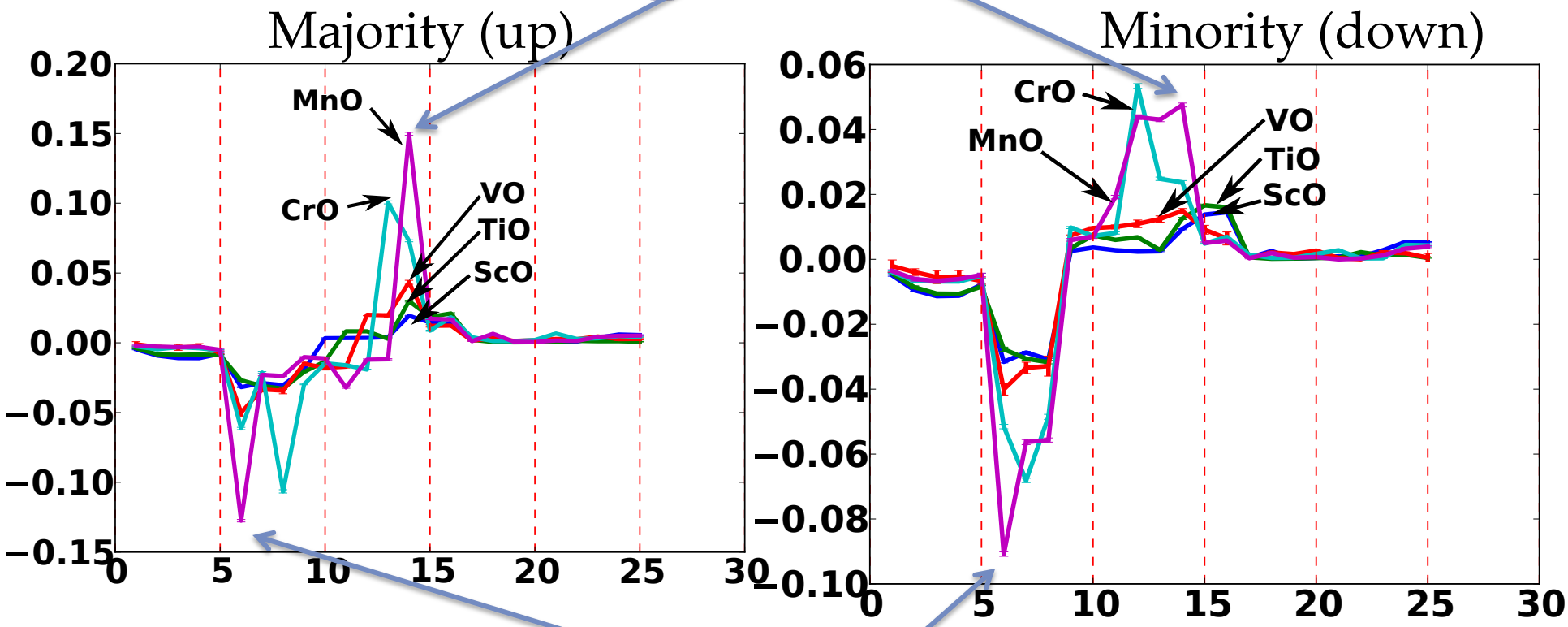


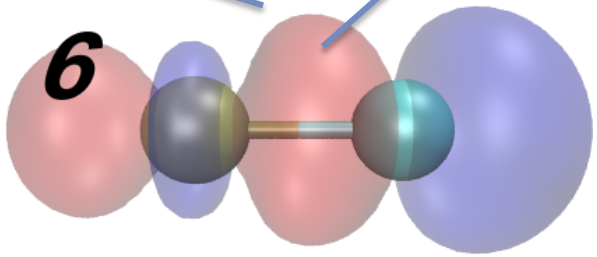
Virtual orbitals

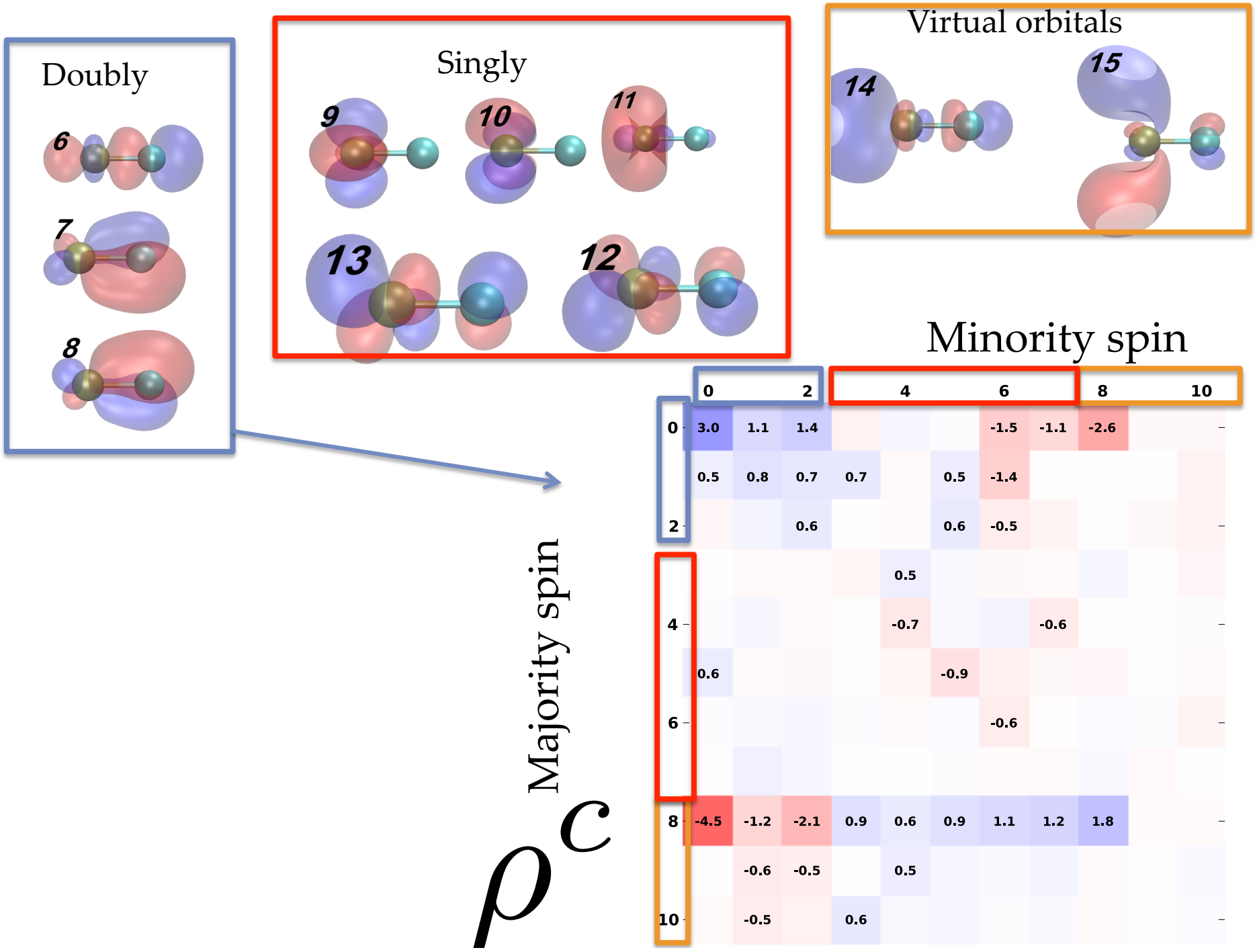


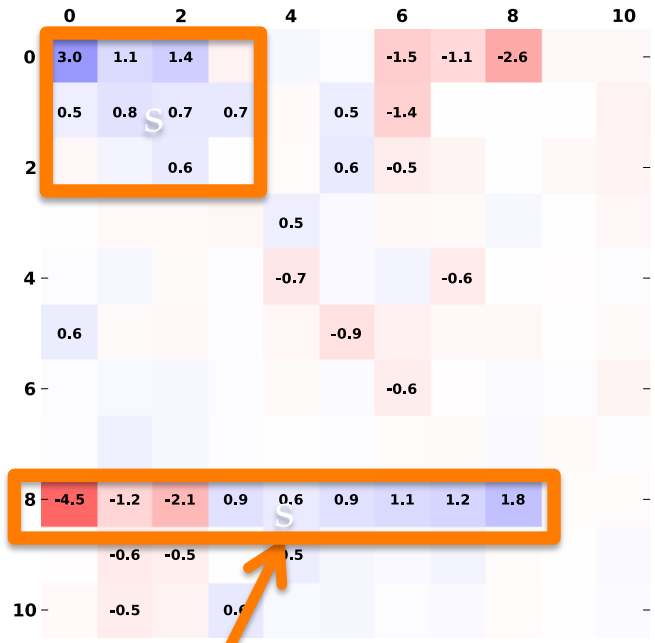
Diagonal of the 1-RDM








Doubly
6
7
8
Singly
9
10
11
13
12
Virtual orbitals
14
15
Minority spin
Majority spin
ρ^c
0 2 4 6 8 10
0 3.0 1.1 1.4 -1.5 -1.1 -2.6
0.5 0.8 0.7 0.7 0.5 -1.4
2 0.6 0.6 -0.5
0.5
4 -0.7 -0.6
0.6 -0.9
6 -0.6
8 -4.5 -1.2 -2.1 0.9 0.6 0.9 1.1 1.2 1.8
-0.6 -0.5 0.5
10 -0.5 0.6



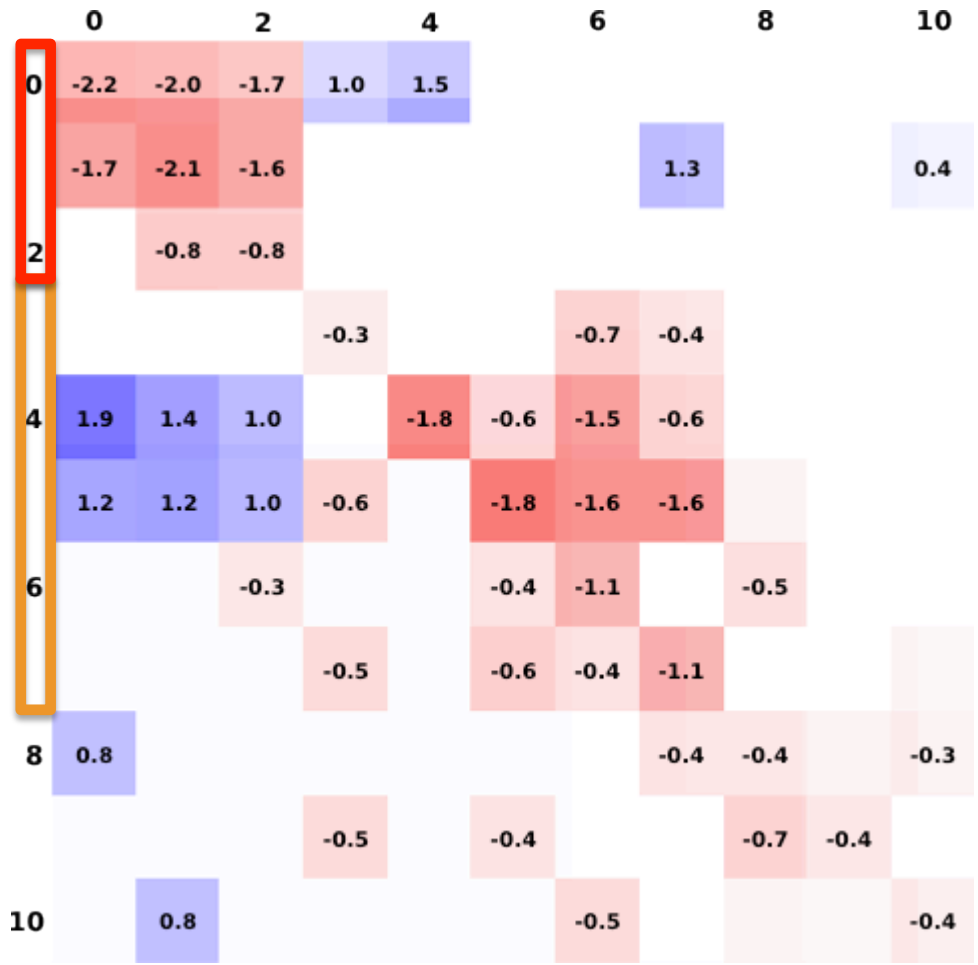
	σ_{dp}	π_{dp}	π_{dp}	σ_d	δ_d	δ_d	π^*_{dp}	π^*_{dp}	σ^*_{dp}
Nominal	2	2	2	1	1	1	1	1	0
Large prob	0	2	2	1	1	1	1	1	2
	0	2	2	2	1	1	1	1	1
	0	2	2	1	2	1	1	1	1
	0	2	2	1	1	2	1	1	1
	0	2	2	1	1	1	2	1	1
	0	2	2	1	1	1	1	2	1

Localized orbitals: MnO

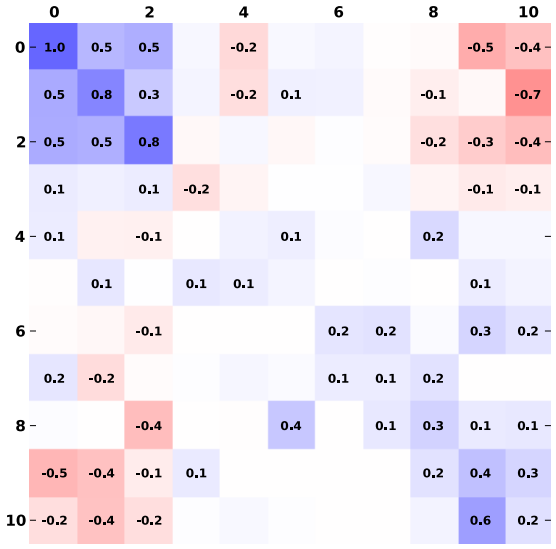
Oxygen centered

TM-centered

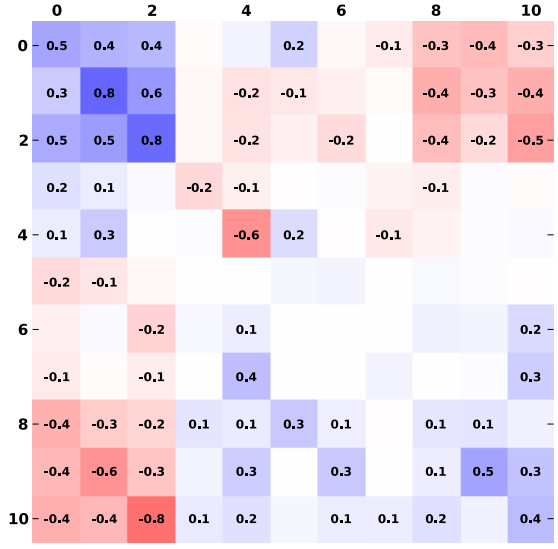
Very clearly left-right correlation!



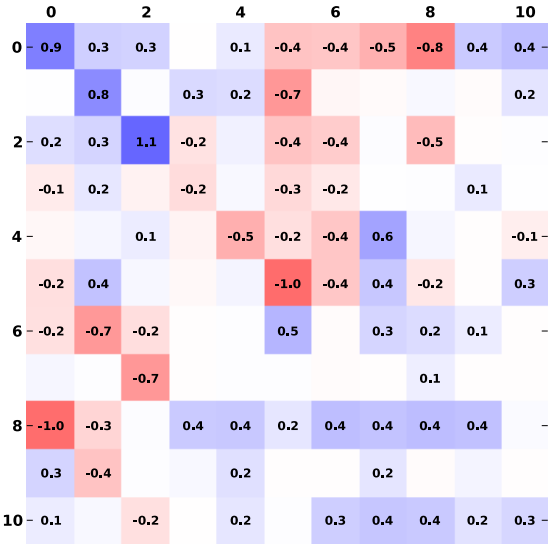
Rho^c for all 5 TM monoxides



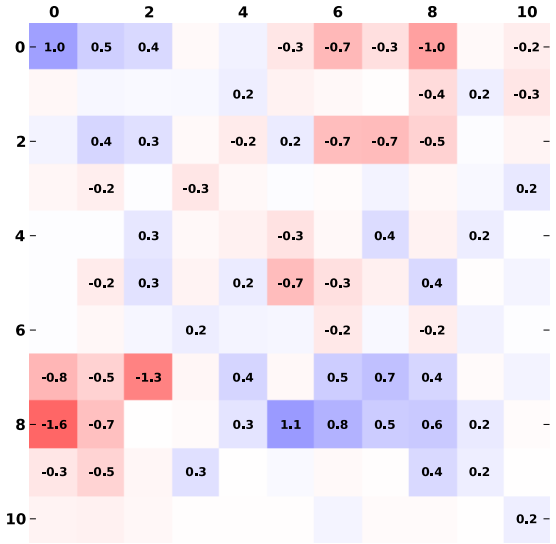
ScO



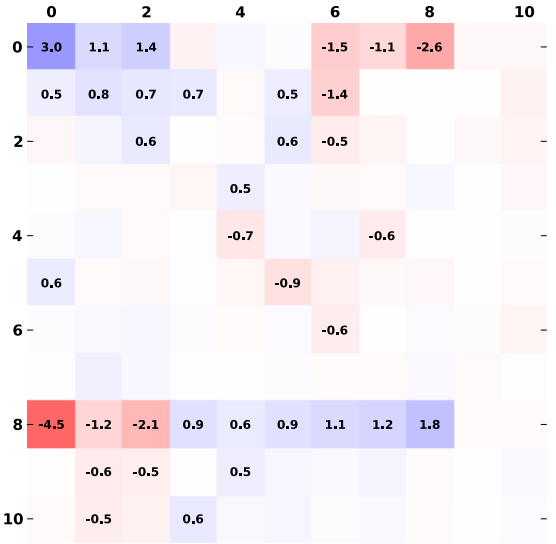
TiO



VO

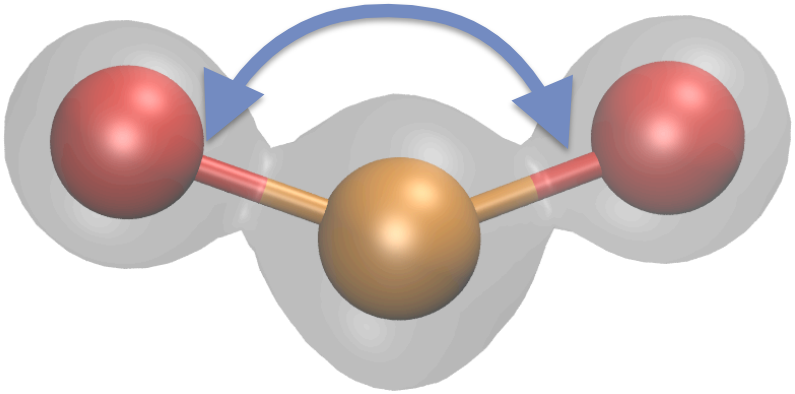


CrO



MnO

TM dioxides: the angle



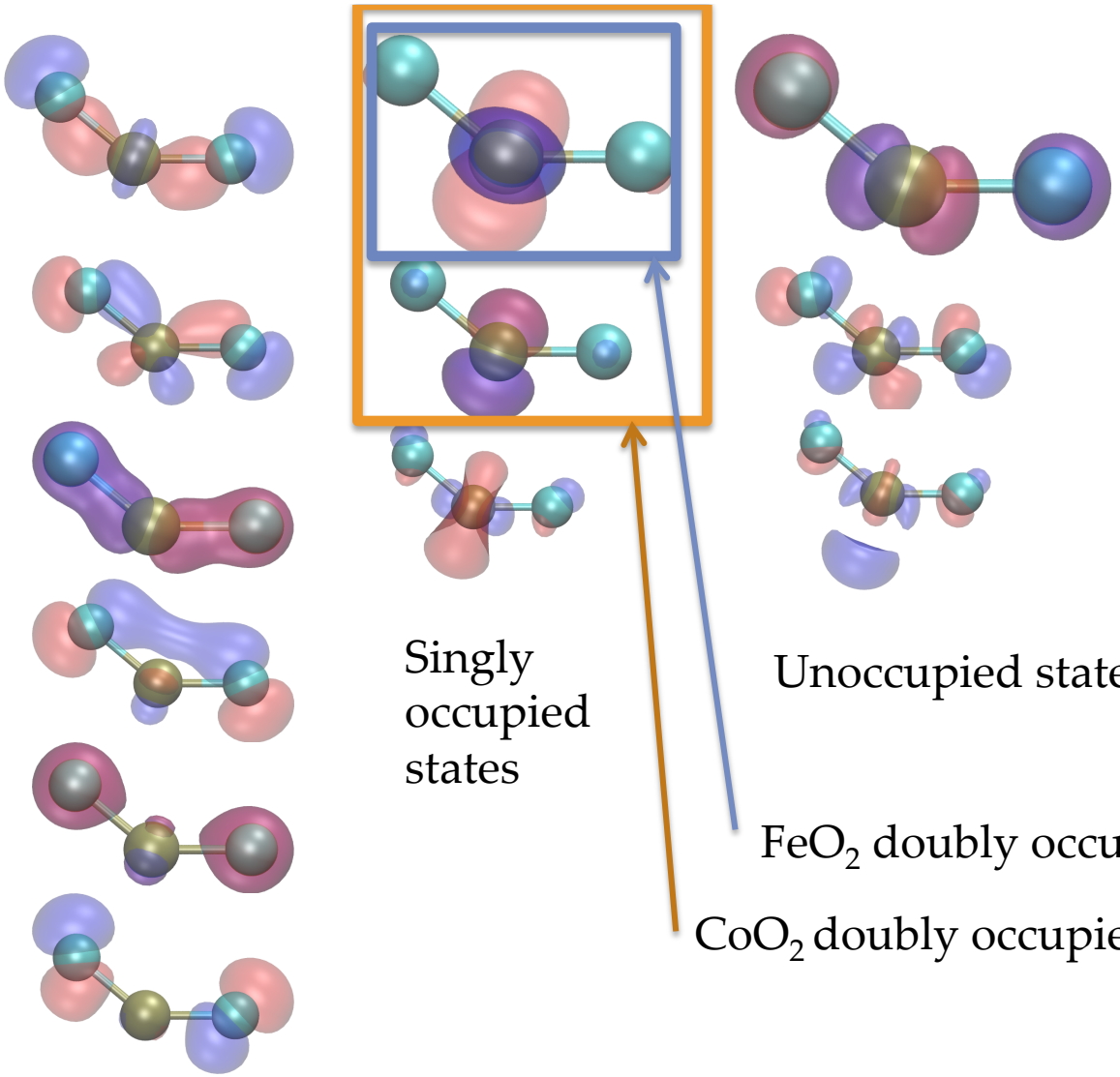
State	DFT	$+U$	$+U\|_{r_0}$	$+U+V$	Expt.
$^4B_1$ MnO_2	128	180	140	143	135 ± 5
$^3B_1$ FeO_2	138	180	155	156	150 ± 10
$^2\Sigma_g^+$ CoO_2	158	180	180	180	180

Kulik & Marzari, J. Chem. Phys. **134,** 094103 (2011)

DMC(SJ) geometries: results

	DFT	DMC(SJ)	Exp
MnO_2	128	140+/-10	135+/-5
FeO_2	138	150+/-10	150+/-10
CoO_2	158	180+/-20	180

TM-O_2: electronic structure



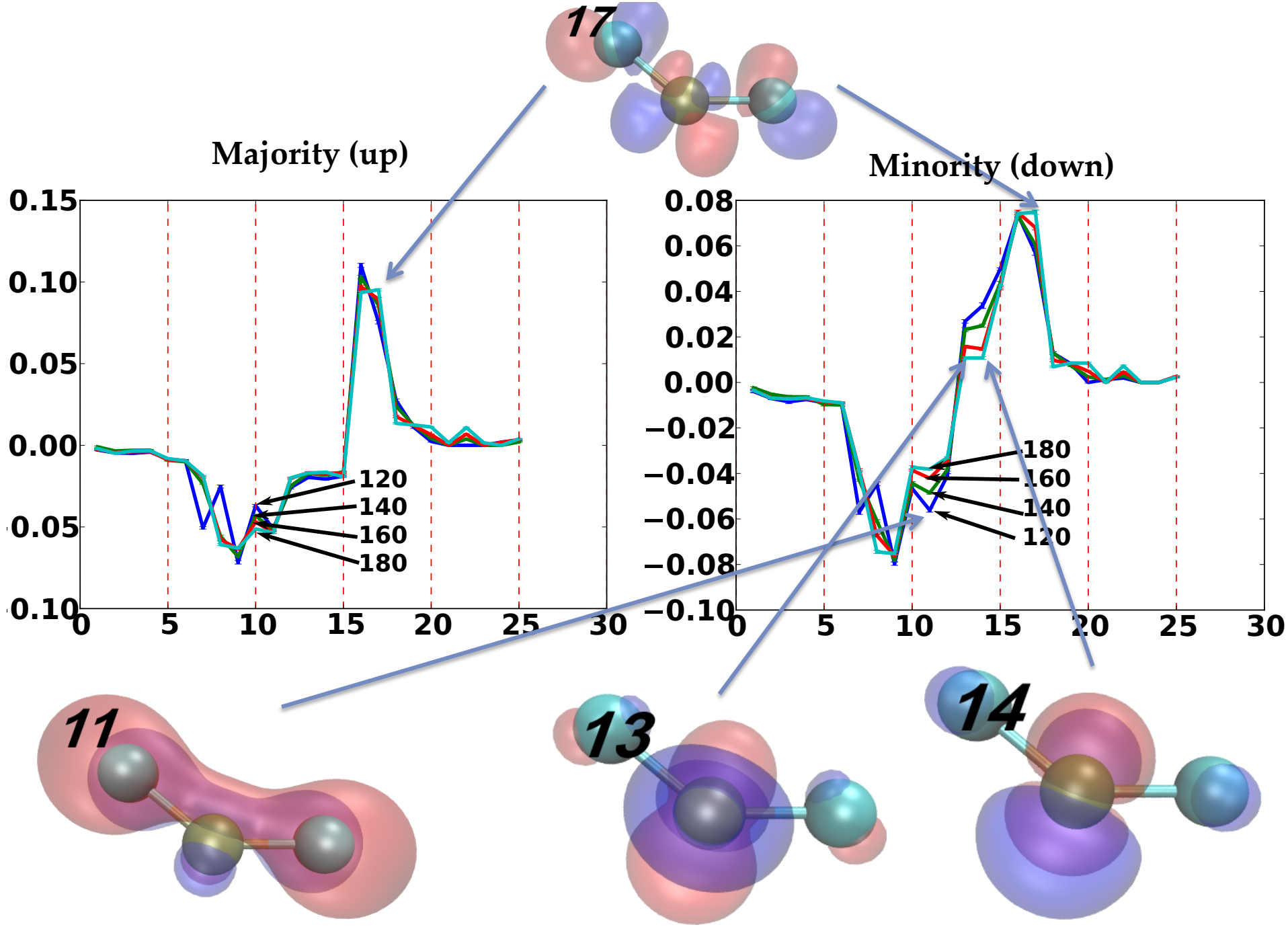
Doubly occupied states

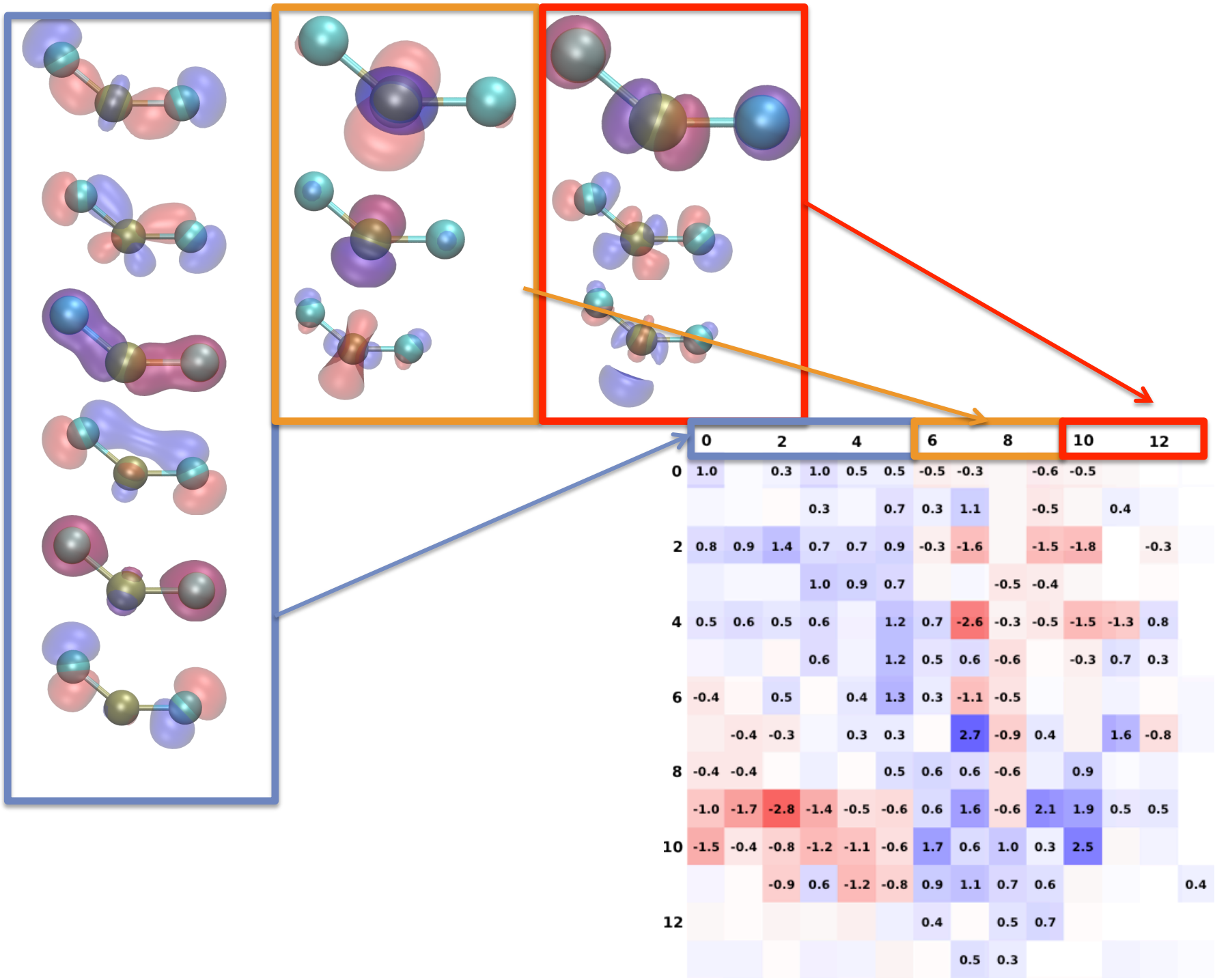
Singly occupied states

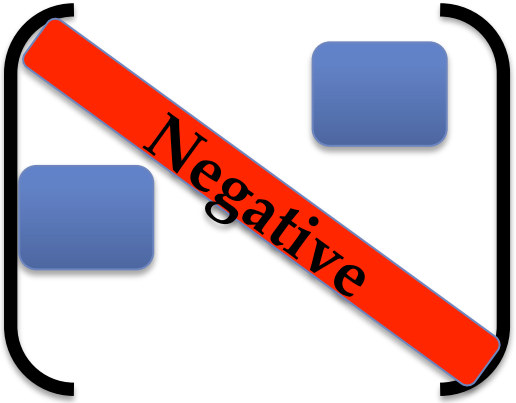
Unoccupied states

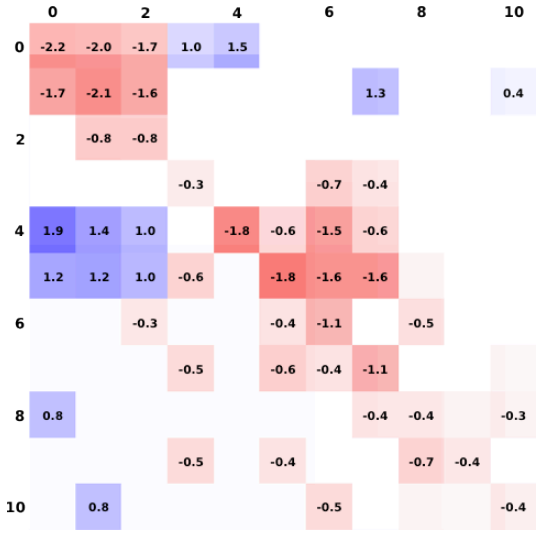
FeO_2 doubly occupies

CoO_2 doubly occupies


17
Majority (up)
Minority (down)
0.15
0.10
0.05
0.00
0.05
0.10
0.08
0.06
0.04
0.02
0.00
−0.02
−0.04
−0.06
−0.08
−0.10
0
5
10
15
20
25
30
120
140
160
180
180
160
140
120
11
13
14


0 2 4 6 8 10 12
0 1.0 0.3 1.0 0.5 0.5 -0.5 -0.3 -0.6 -0.5
0.3 0.7 0.3 1.1 -0.5 0.4
2 0.8 0.9 1.4 0.7 0.7 0.9 -0.3 -1.6 -1.5 -1.8 -0.3
1.0 0.9 0.7 -0.5 -0.4
4 0.5 0.6 0.5 0.6 1.2 0.7 -2.6 -0.3 -0.5 -1.5 -1.3 0.8
0.6 1.2 0.5 0.6 -0.6 -0.3 0.7 0.3
6 -0.4 0.5 0.4 1.3 0.3 -1.1 -0.5
-0.4 -0.3 0.3 0.3 2.7 -0.9 0.4 1.6 -0.8
8 -0.4 -0.4 0.5 0.6 0.6 -0.6 0.9
-1.0 -1.7 -2.8 -1.4 -0.5 -0.6 0.6 1.6 -0.6 2.1 1.9 0.5 0.5
10 -1.5 -0.4 -0.8 -1.2 -1.1 -0.6 1.7 0.6 1.0 0.3 2.5
-0.9 0.6 -1.2 -0.8 0.9 1.1 0.7 0.6 0.4
12 0.4 0.5 0.7
0.5 0.3





Symmetric left-right correlation

Enabled by partial d occupation

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