DFT+DMFT and its Discontents: towards a first-principles theory of correlated electron materials

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Hyowon Park, Andrew J. Millis, and Chris A. Marianetti, PRL 109, 156402 (2012)
E. Gull, O. Parcollet and A. J. Millis, PRL 110 216406 (2013)
H. T. Dang, A. J. Millis and C. Marianetti, arXiv:1309.2995

ICAM/BU 2013

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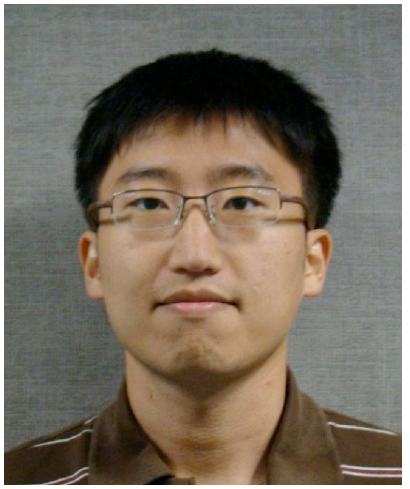
Collaborators

C. Marianetti (Columbia)

Hung The Dang (Columbia->Aachen)

Ara Go (Columbia)

***Hyowon Park (Columbia)**



M-J. Han (CU->ANL->KAIST)
X. Wang (CU->U-Md)
L. deMedici (ESPCI)

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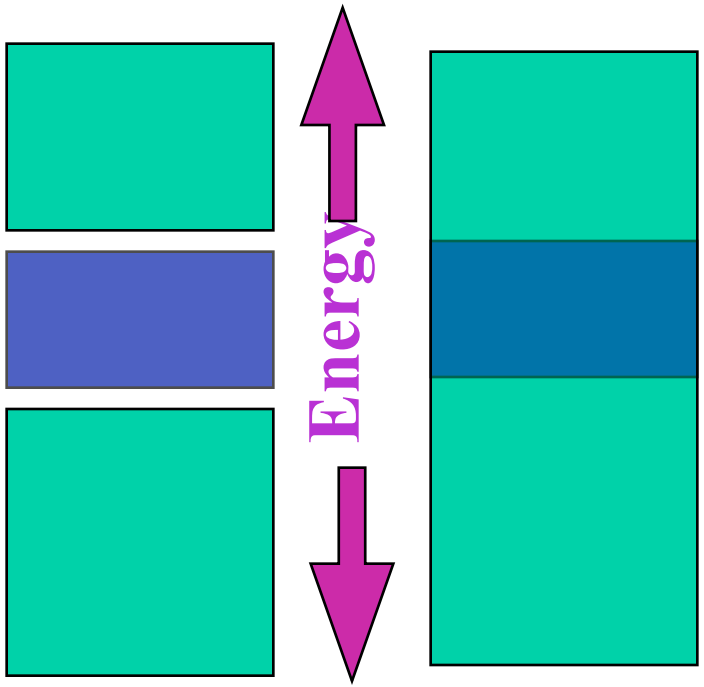
General Approach to Many-Body Electronic Structure

- =>partition d.o.f. into ``correlated subspace'' (active space) and ``background''

- treat correlated subspace by many-body method; treat background by mean field method

- embed active space into background



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DFT+DMFT

1. background electronic structure (DFT)
2. Active subspace: (atomic-like d-orbitals)
3. On-site intra-d interactions (c-RPA)
4. Solve active space (DMFT--single-site)
5. Embed (double counting and charge self-consistency)

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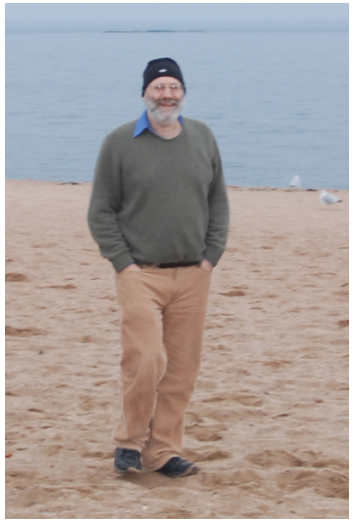
The most important recent developments: I



Gabi Kotliar

Dynamical Mean Field Theory

Enables marriage of many-body and real-materials theory

Antoine Georges

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DMFT

Physical model: M (typically infinity) orbitals in Hilbert space

Parametrize self energy in terms of small number N of functions of frequency.

$$\Sigma(\mathbf{k},\omega) = \sum_{a} \mathbf{f}(\mathbf{k})_{\mathbf{a}}\, \Sigma^{\mathbf{a}}_{\mathbf{DMFT}}(\omega) \qquad \mathbf{a} = 1 \ldots \mathbf{N}$$

$\Sigma^{\mathbf{a}}_{\mathbf{DMFT}}$ **is self energy of a 0 (space) + 1 (time)d QFT**

parametrization function f determines 'flavor' of DMFT

N->M; recover exact theory.

?Can we solve the theory with any (useful) N?

?Can we get reasonable results with reasonable N?

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The most important recent developments: II

Philipp Werner

Continuous-Time Quantum Monte Carlo

Enables solution of DMFT equations in realistic contexts

Field started by Rubtsov,
important contributions from Haule

Emanuel Gull

P. Werner, A Comanac, Luca De Medici, M. Troyer, and A.Millis, PRL **97**, 076405 (2006).
E. Gull, P. Werner, O. Parcollet and M. Troyer, EPL 82 57003 (2008).

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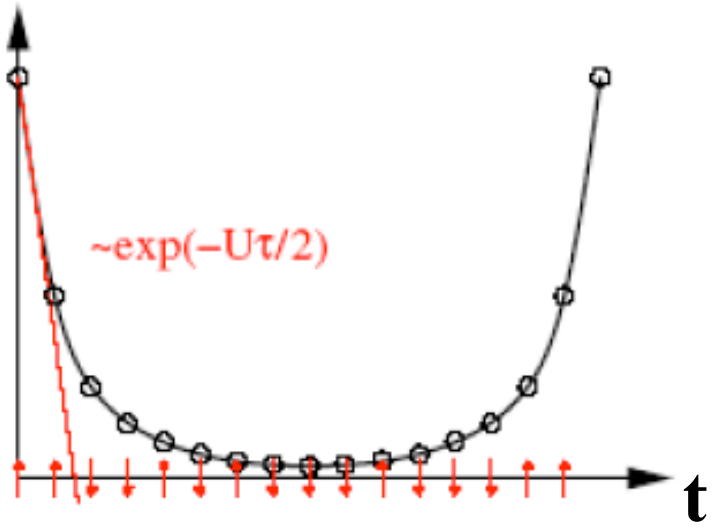
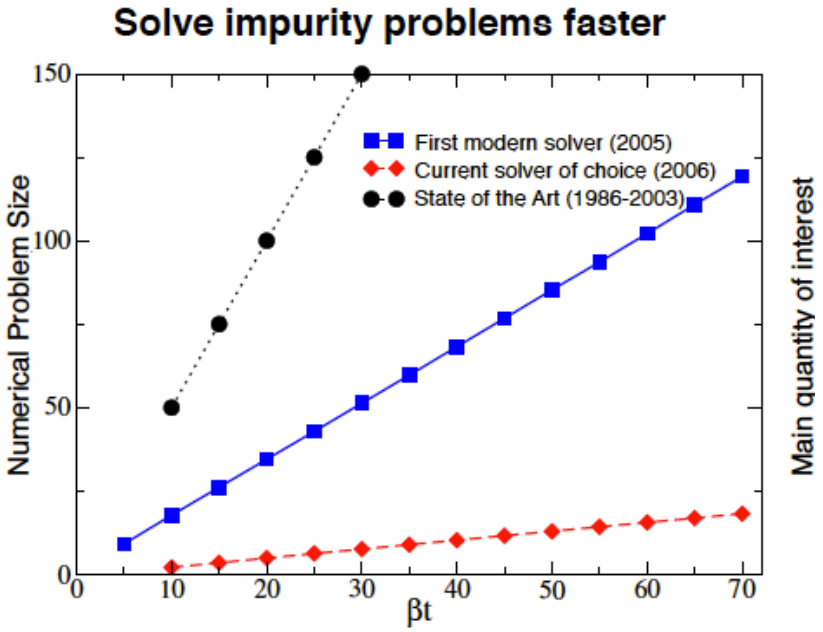
CT-QMC

CT-QMC: ``many-body adaptive grid”



All methods involve manipulating matrices; cost ~cube of matrix size.



- For the same problem: problem size reduced by ~30.
- Corresponds to time speedup of factor 30^3 = 27’000 or ~25 years of Moore’s law

(Image from From E. Gull)

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A model system

$$\mathbf{H} = -\sum_{ij} t_{i-j} c^{\dagger}_{i\sigma} c_{j\sigma} + U \sum_{i} n_{i\uparrow} n_{i\downarrow}$$

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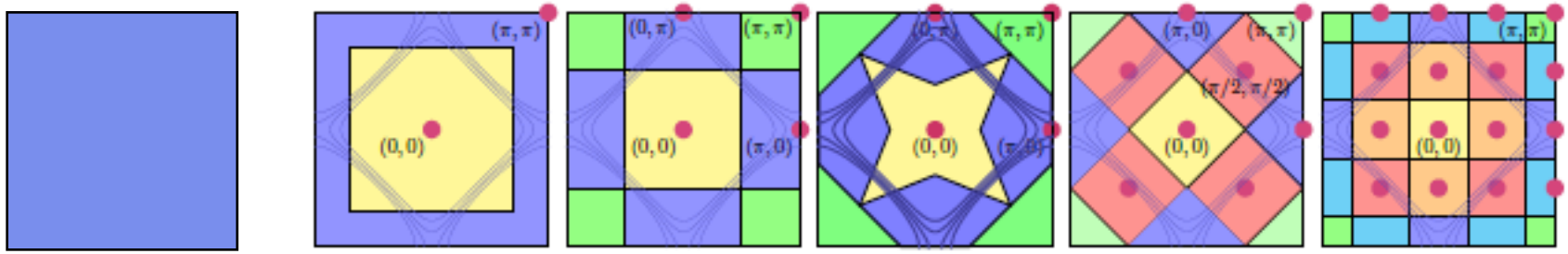
Validation

(cluster) dmft: approximation to many body problem: accuracy controlled by parameter N. Example:



$$\Sigma_{\mathbf{p}}(\omega) \rightarrow \Sigma_{\mathbf{p}}^{\mathbf{approx}}(\omega) = \sum_{\mathbf{a}} \phi_{\mathbf{a}}(\mathbf{p}) \Sigma_{\mathbf{a}}(\omega)$$

$\phi_{\mathbf{a}}(\mathbf{p}) = 1$ **if p is in the patch containing** $\mathbf{K_a}$ **and is 0 otherwise**

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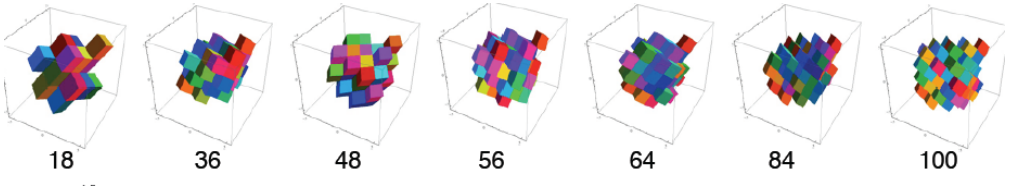
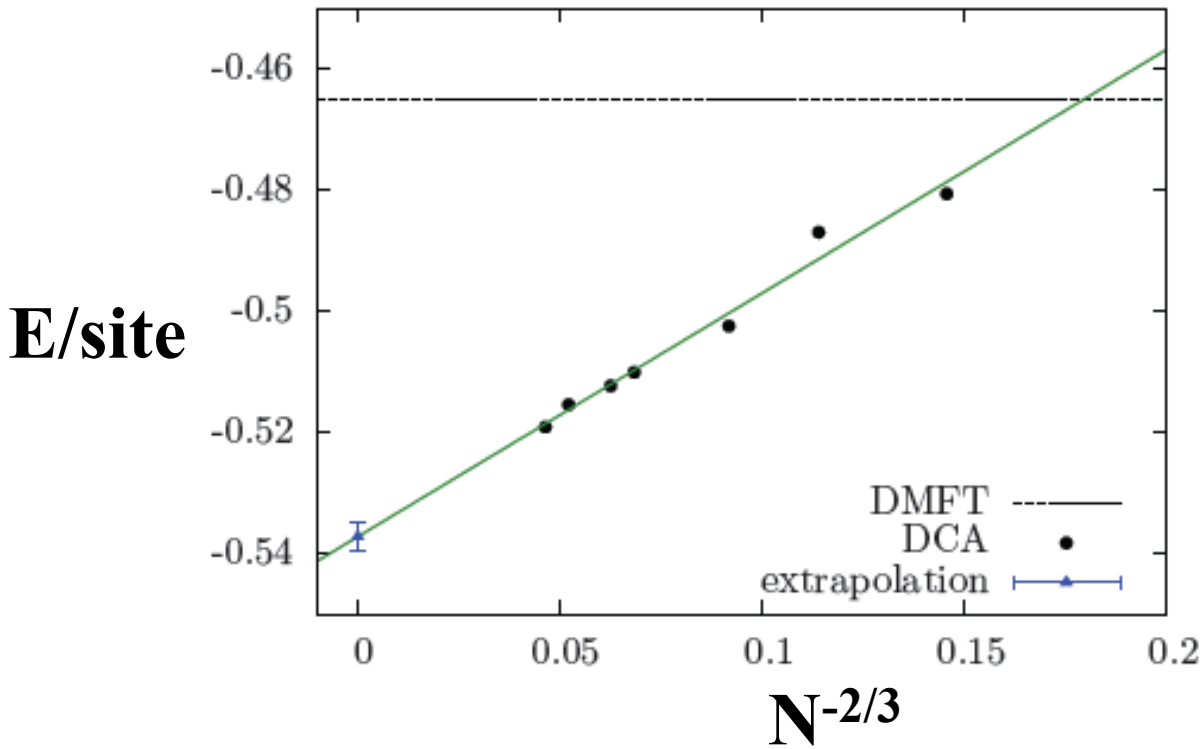
Validation

3D Hubbard model,
n=1 U=8t=2W/3 T=0.4t





Fuchs, **Gull**, et al PRL 106 030401 (2011)

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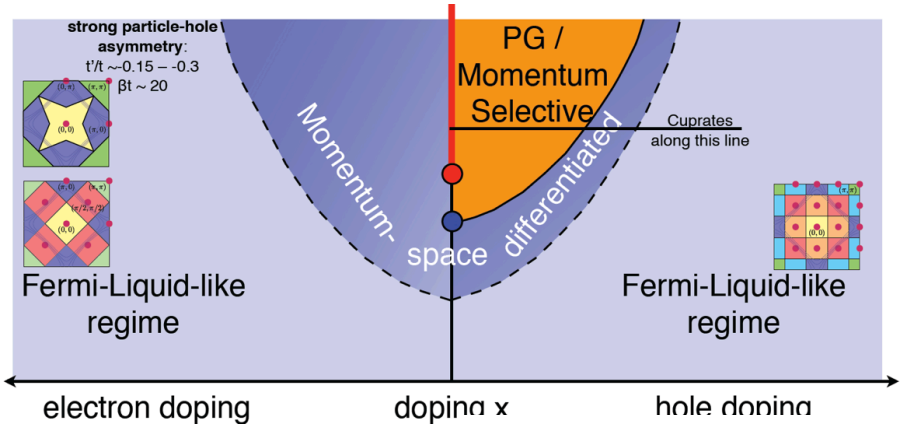
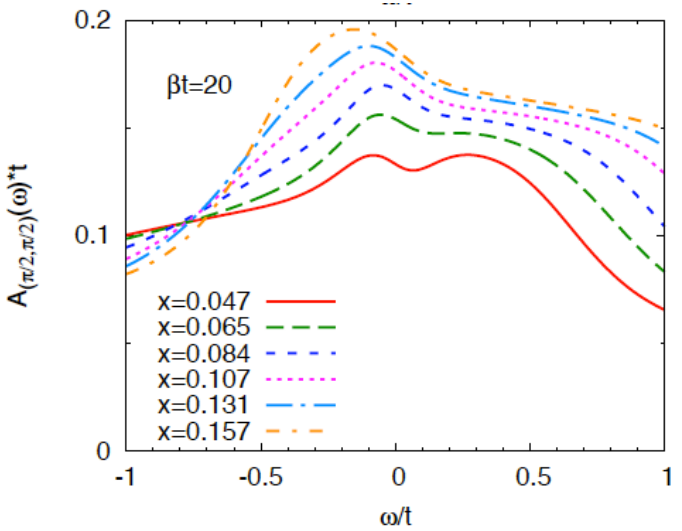
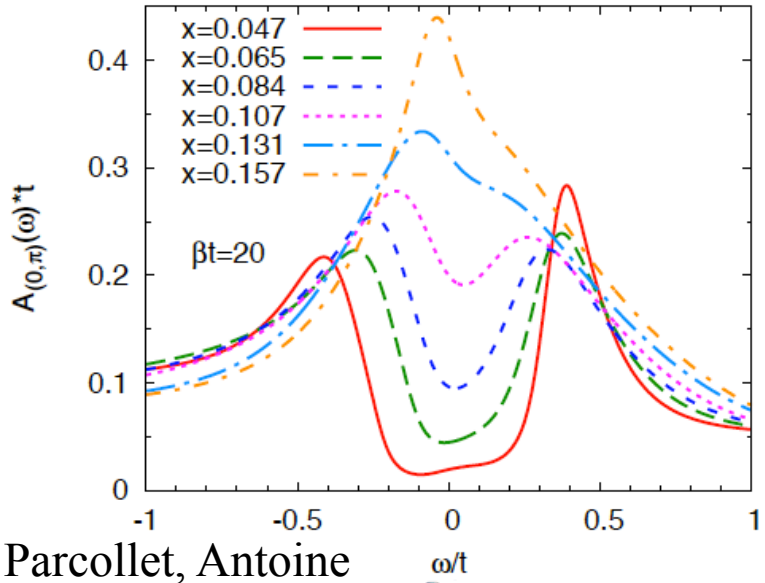
Particle-hole asymmetric pseudogap in 2d Hubbard model







Emanuel Gull, Michel Ferrero, Olivier Parcollet, Antoine Georges, A J. M, Phys. Rev. B82 155101 (2010).

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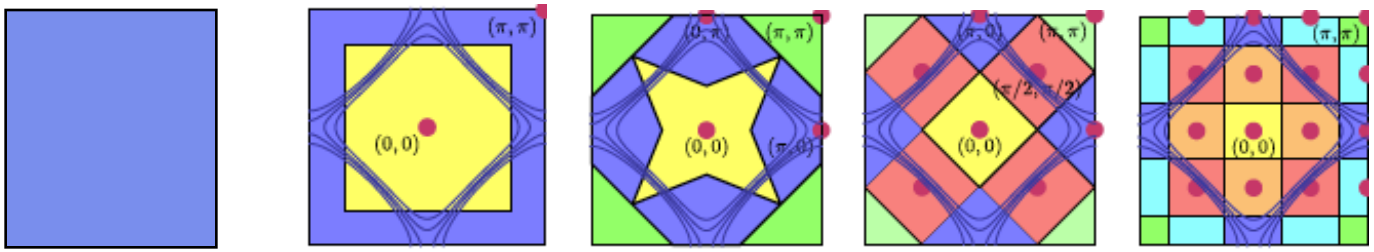
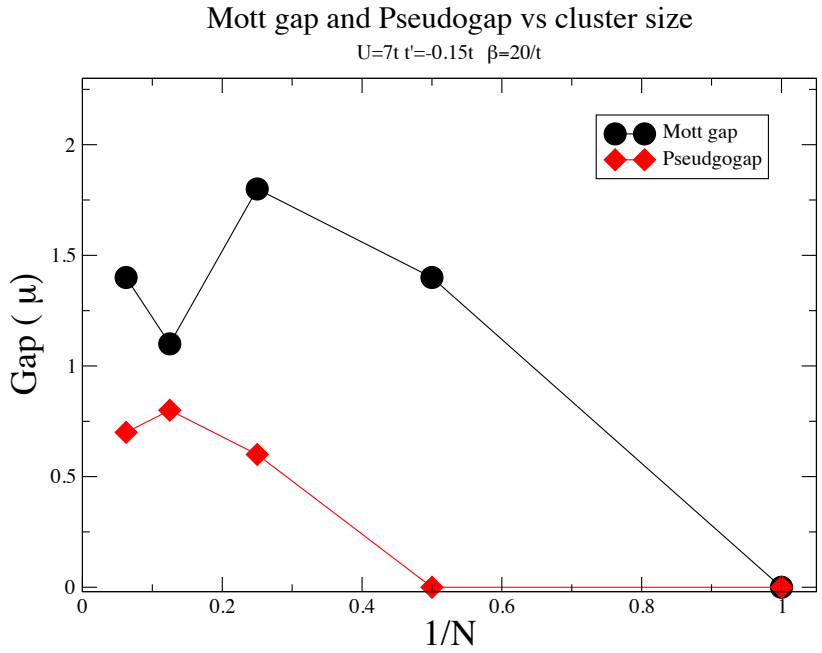
Particle-hole asymmetric pseudogap in 2d Hubbard model





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superconductivity and the pseudogap in the 2D Hubbard model

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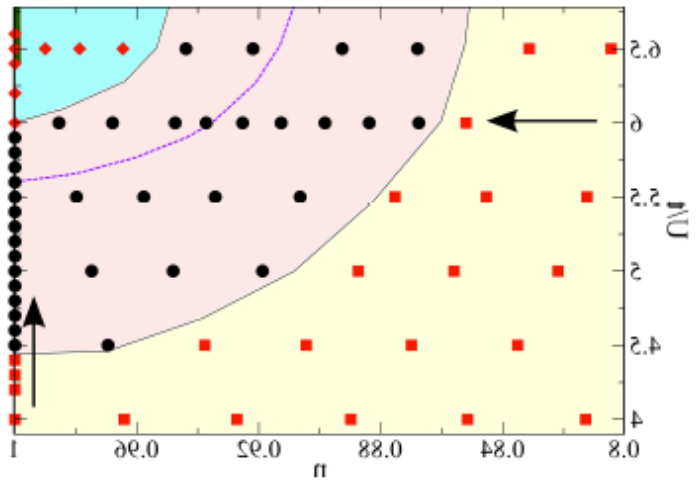

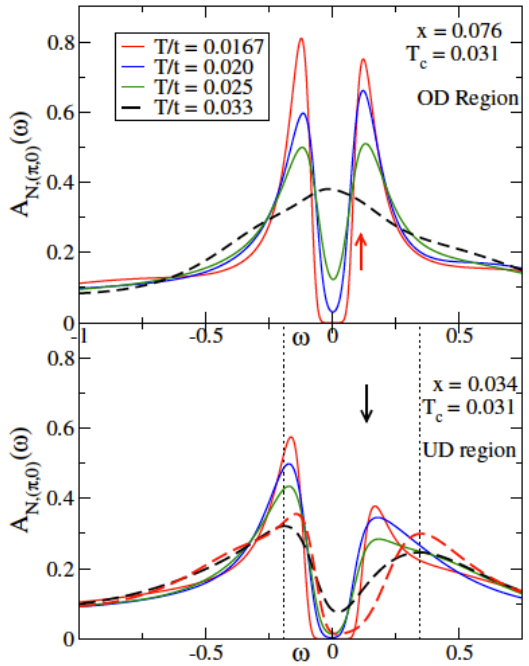

E. Gull, O. Parcollet and A. J. Millis, PRL 110 216406 (2013)

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Summary: Hubbard model

The method works for a model system

--gives physically interesting answers

--theoretically reasonable convergence structure

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Beyond model systems (DFT+DMFT)

Introduced by Liechtenstein, Anisimov, Georges, Kotliar....

now widely used..

Our recent work

*Xin Wang, M. J. Han, Luca de' Medici, Hyowon Park, C. A. Marianetti and Andrew J. Millis, Physical Review **B86**, 195136 (2012).
*H. T. Dang and AJM Phys. Rev. B87, 155127 (2013), Phys. Rev. B87184434 (2013)
*H. T. Dang, A. J. Millis and C. Marianetti, arXiv:1309.2995

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an application: ferromagnetism in vanadate superlattices

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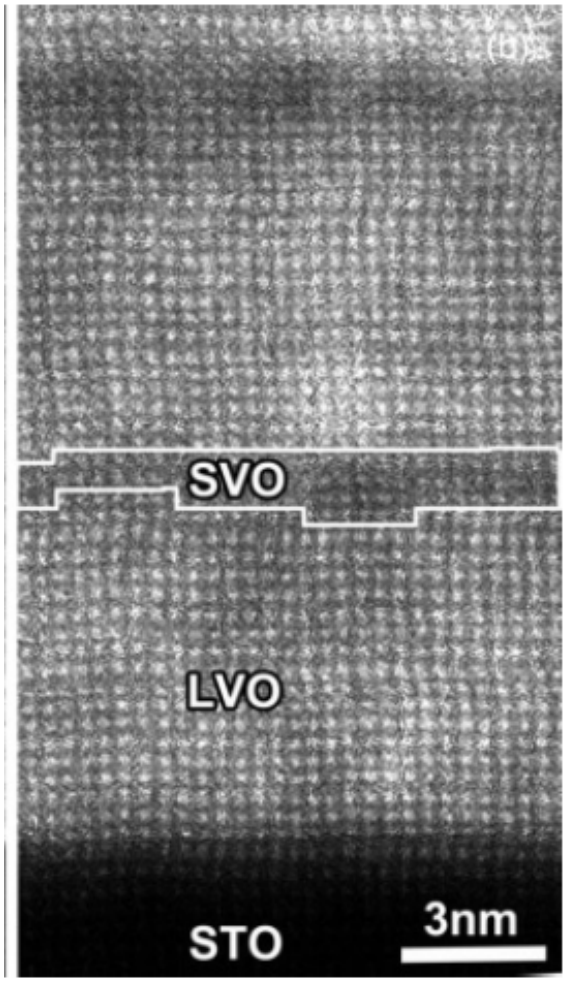
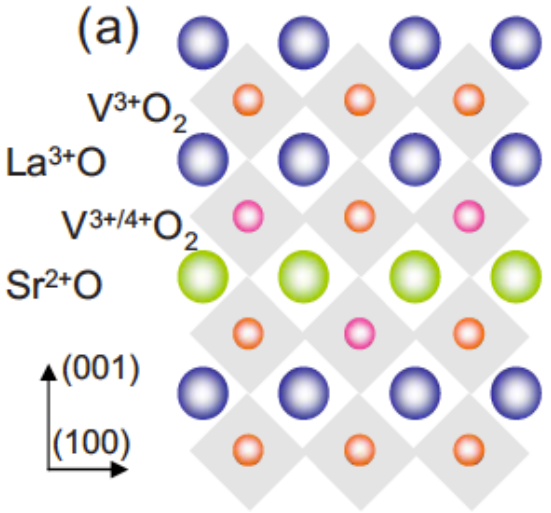
Vanadate quantum well

$(LaVO_3)_n/(SrVO_3)_m$



$LaVO_3$: Antiferromagnetic Mott insulator (d^2)

$SrVO_3$: correlated metal (d^1)



Luders et al Phys Rev B80 241102 (2009) and Boulay et al Phys Rev B83 125403 (2011)

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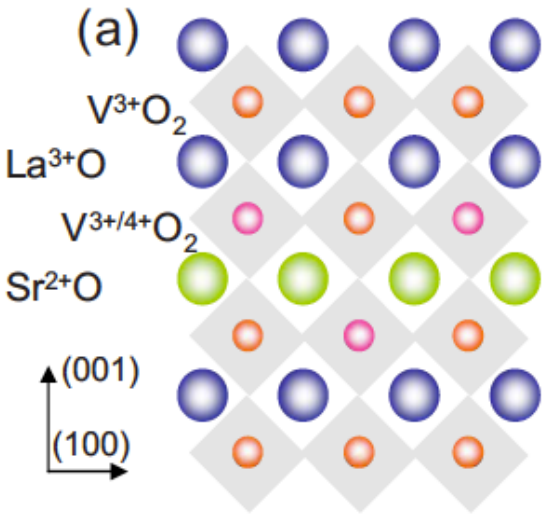
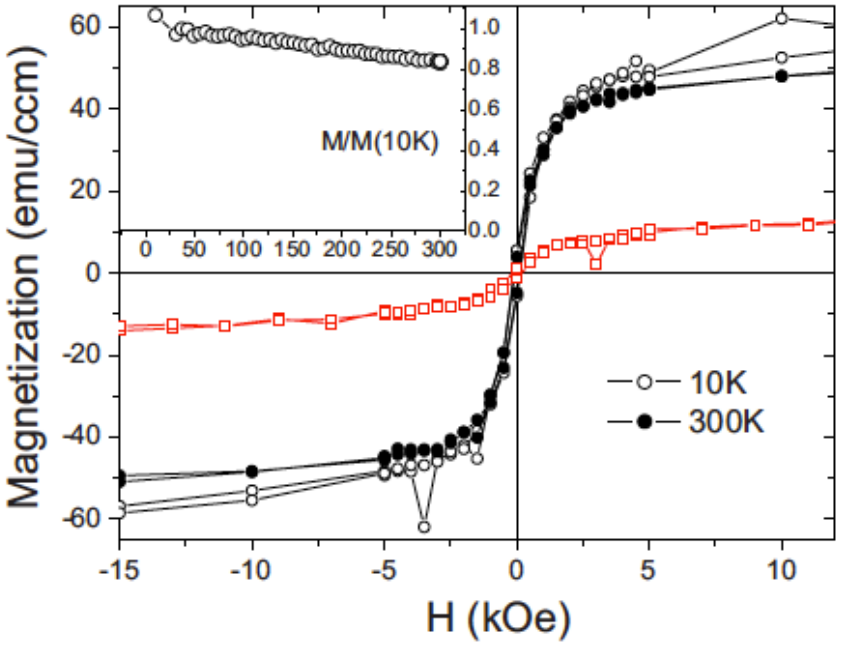
Superlattice: room T ferromagnetism!

$(LaVO_3)_n/(SrVO_3)_1$





Luders et al Phys Rev B80 241102 (2009)

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Experimental situation complicated

Theoretical Questions are clear

(1) The design rule question: can theory reliably identify the circumstances under which a material will exhibit a new phase (magnetic, superconducting, insulating...) or an optimized version of an existing phase

(0) The modelling question: can theory reliably obtain the values of physical quantities--gaps, transition temperatures, charge transfers.....

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Design Rules

***Qualitative: identify important features/trends**

***Quantitative: predict T_c or at least sign of T_c**

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Qualitative Design Rules: limitations of reasoning by analogy

High-T_c copper-oxide superconductivity

***One band**
***Proximity to Mott phase**
***S=1/2**

High-T_c iron-pnictide superconductivity

***Several bands**
***Proximity to metallic SDW**
***`Hunds metal' (local spin S>1/2)**

Theory needed, even for qualitative trends

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***Theory needed**
***Density functional band theory (at least in its present implementation) inadequate**
***Complete solution of all-electron correlation problem is impossible**

=> need to
(1) Identify subset of orbitals to be correlated
(2) Solve correlation problem
(3) Embed solution in wider electronic structure.

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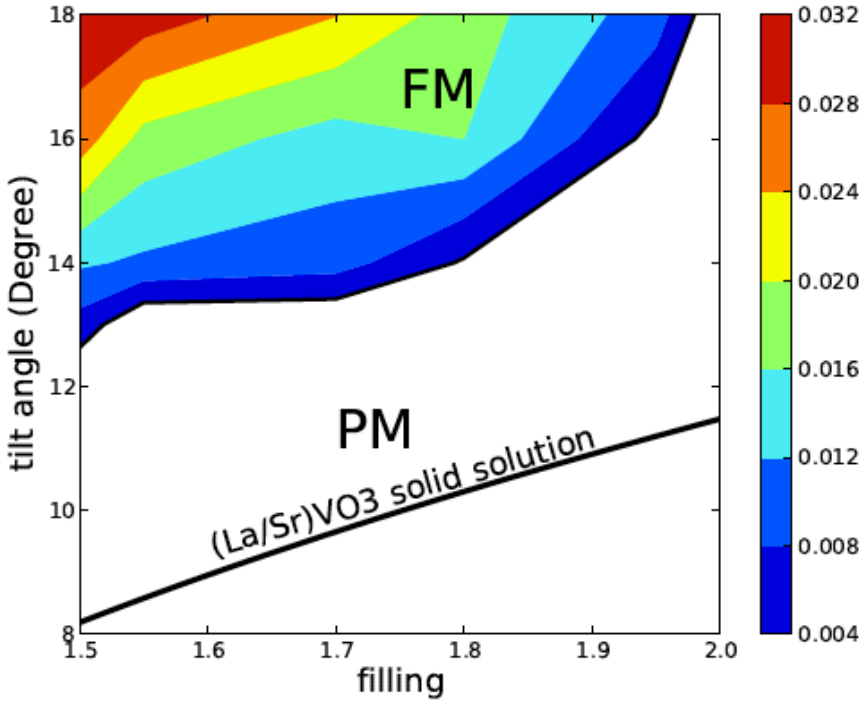
DFT+DMFT La/$SrVO_3$

Key feature: rotations of VO_3 octahedron

Bulk La/$SrVO_3$



Ferromagnetism favored by large tilts, distance from AF Mott insulator

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DFT+DMFT La/$SrVO_3$

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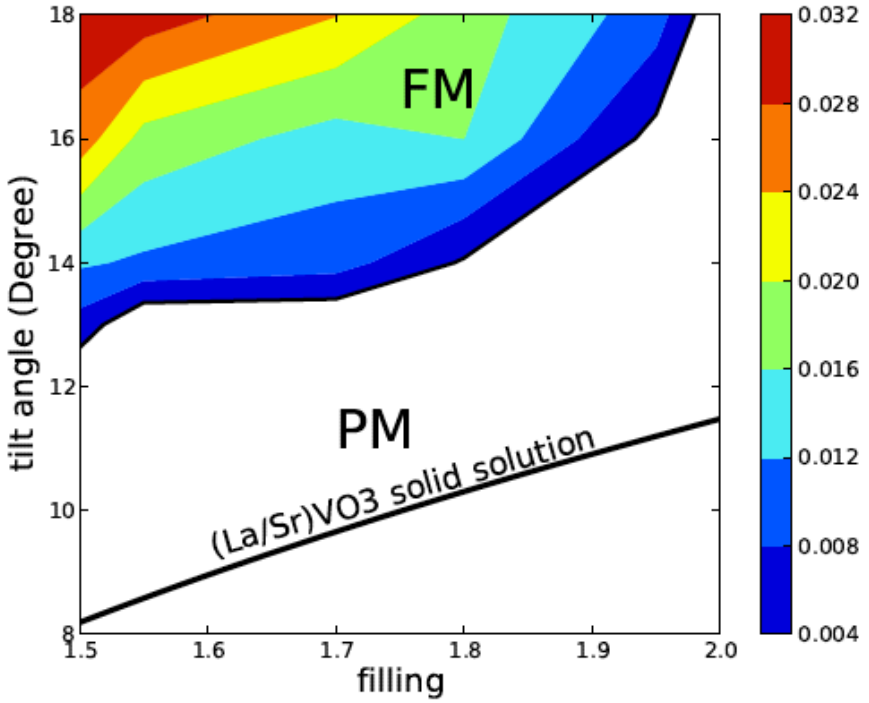

In LVO/SVO solid solutions, doping away from Mott insulator also moves tilt angle in wrong way!

What about superlattices?

Ferromagnetism favored by large tilts, distance from AF Mott insulator

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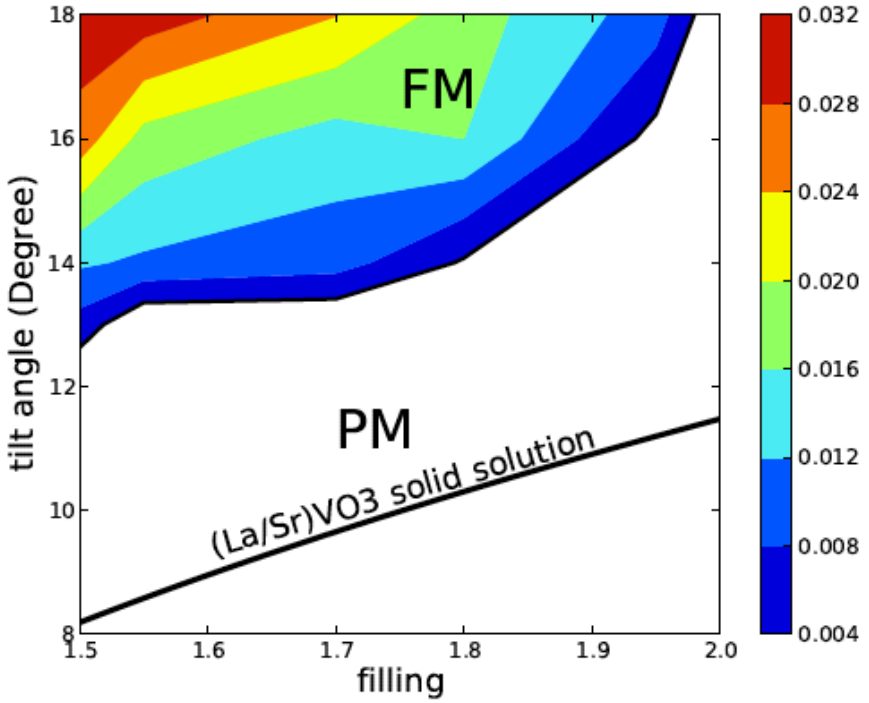
DFT+DMFT La/$SrVO_3$

Key feature: rotations of VO_3 octahedron

Bulk La/$SrVO_3$



In a superlattice, carrier concentration and tilt may be independently controlled

=>

? move into magnetic regime?

Ferromagnetism favored by large tilts, distance from AF Mott insulator

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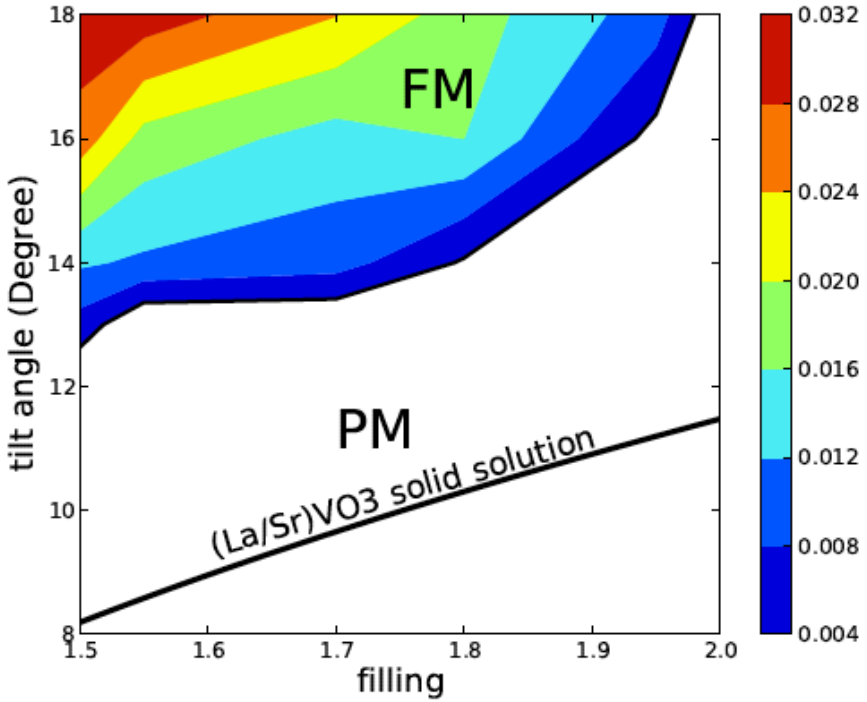
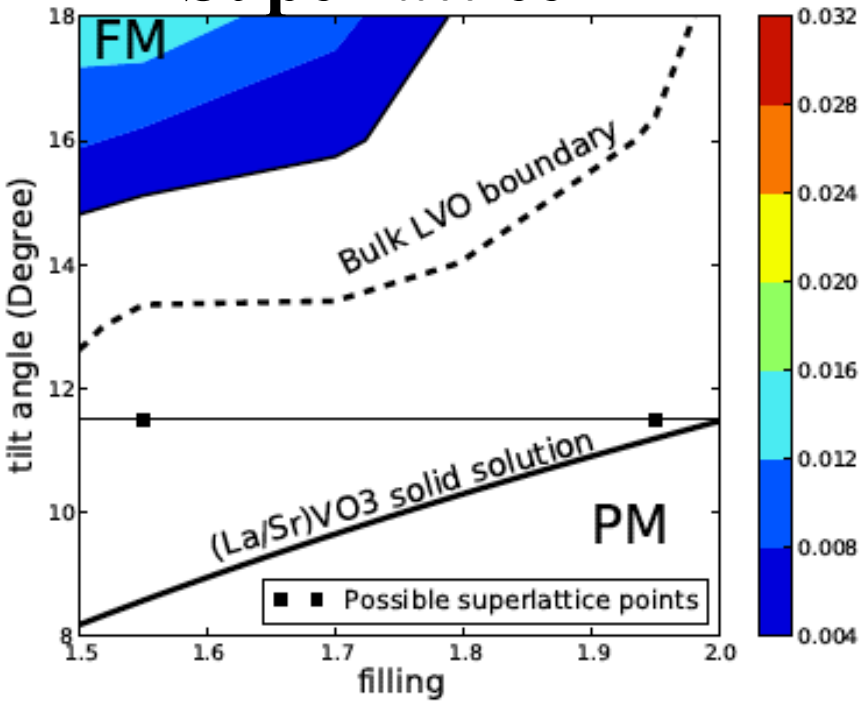
DFT+DMFT La/$SrVO_3$

Key feature: rotations of VO_3 octahedron

Bulk La/$SrVO_3$



Superlattice



!!Superlattice moves tilts in the wrong way!!

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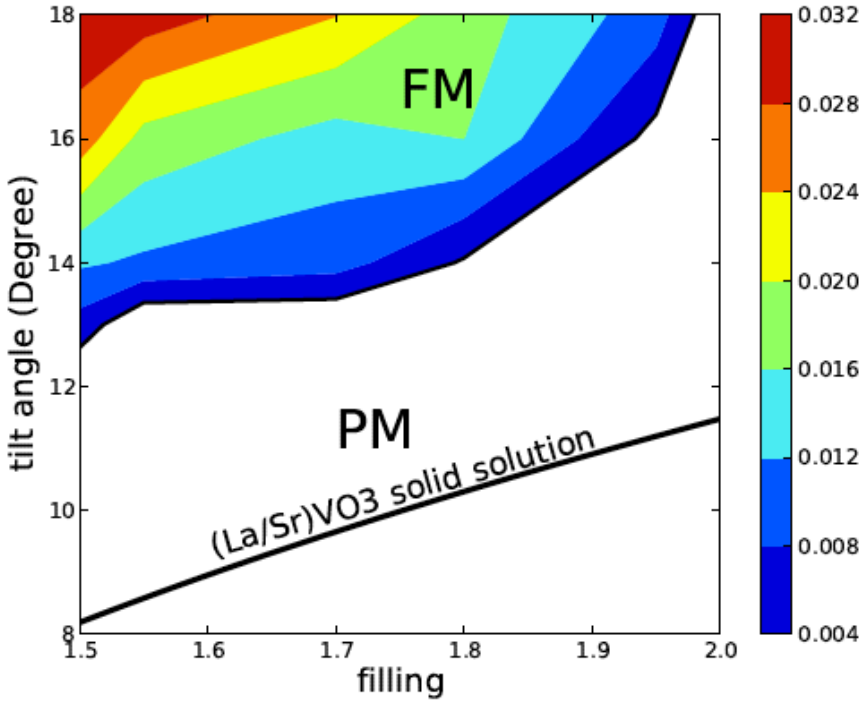
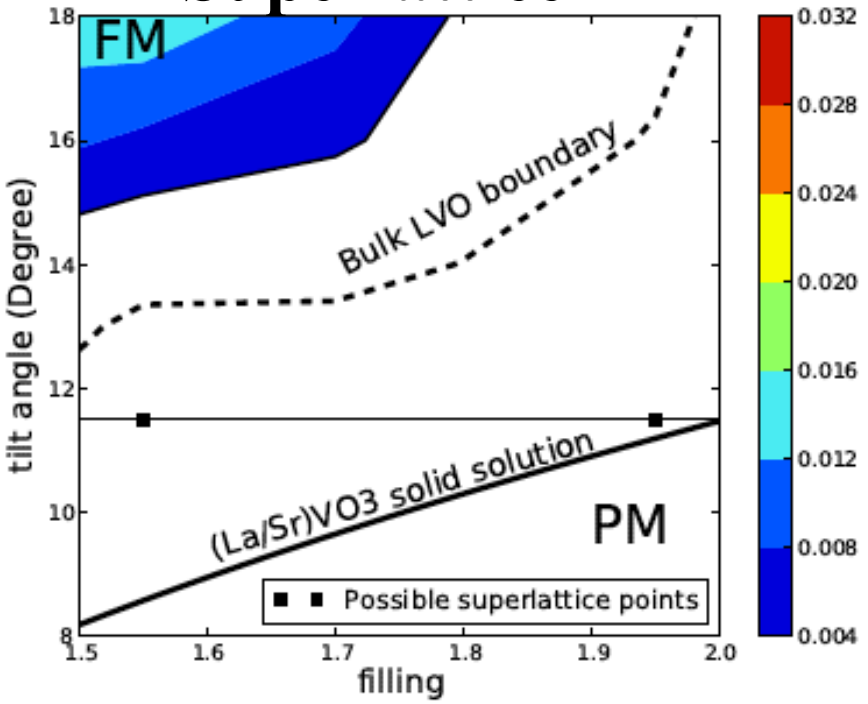
DFT+DMFT La/$SrVO_3$

Key feature: rotations of VO_3 octahedron

Bulk La/$SrVO_3$



Superlattice



!!Superlattice moves tilts in the wrong way!!

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Unsatisfactory aspect of theory

many moving parts

=>

?are we doing the right thing?

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DFT+DMFT

1. background electronic structure (DFT)
2. Active subspace: (atomic-like d-orbitals)
3. On-site intra-d interactions (c-RPA)
4. Solve active space (DMFT--single-site)
5. Embed (double counting and charge self-consistency)

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the loop

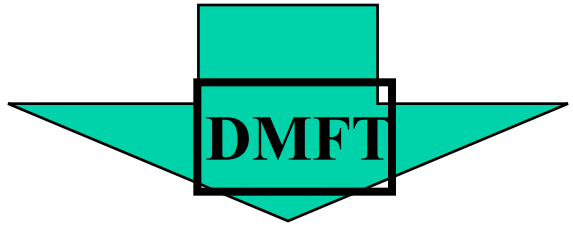
Onsite U, J pre-computed

$$\rho(\mathbf{r}) \Rightarrow \mathbf{V_{Kohn-Sham}}(\mathbf{r}) \Rightarrow \mathbf{G_0}(\mathbf{r},\mathbf{r}';\omega)$$

Charge self consistency

Double counting shift

$$\rho(\mathbf{r}) = \int \frac{\mathbf{d}\omega}{\pi} \mathbf{f}(\omega)\mathbf{G}(\mathbf{r},\mathbf{r};\omega)$$



$$\hat{\mathbf{\Sigma}} = |\mathbf{d}> \mathbf{\Sigma}(\omega) < \mathbf{d}|$$

$$\mathbf{G}(\mathbf{r},\mathbf{r}';\omega) = \left(\mathbf{G_0}(\mathbf{r},\mathbf{r}';\omega)^{-1} - \hat{\mathbf{\Sigma}}(\omega)\right)^{-1}$$

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We tried this out

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We tried this out

Material	Expt	Th

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We tried this out

Material	Expt	Th
$SrVO_3$		

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We tried this out

Material	Expt	Th
$SrVO_3$	M	

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We tried this out

Material	Expt	Th
$SrVO_3$	M	M

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We tried this out

Material	Expt	Th
$SrVO_3$	M	M
$LaTiO_3$		

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We tried this out

Material	Expt	Th
$SrVO_3$	M	M
$LaTiO_3$	I	

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We tried this out

Material	Expt	Th
$SrVO_3$	M	M
$LaTiO_3$	I	M

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We tried this out

Material	Expt	Th
$SrVO_3$	M	M
$LaTiO_3$	I	M
$LaVO_3$		

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We tried this out

Material	Expt	Th
$SrVO_3$	M	M
$LaTiO_3$	I	M
$LaVO_3$	I	

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We tried this out

Material	Expt	Th
$SrVO_3$	M	M
$LaTiO_3$	I	M
$LaVO_3$	I	M

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We tried this out

Material	Expt	Th
$SrVO_3$	M	M
$LaTiO_3$	I	M
$LaVO_3$	I	M
La_2CuO_4		

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We tried this out

Material	Expt	Th
$SrVO_3$	M	M
$LaTiO_3$	I	M
$LaVO_3$	I	M
La_2CuO_4	I	

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We tried this out

Material	Expt	Th
$SrVO_3$	M	M
$LaTiO_3$	I	M
$LaVO_3$	I	M
La_2CuO_4	I	M

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We tried this out

Material	Expt	Th
$SrVO_3$	M	M
$LaTiO_3$	I	M
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La_2CuO_4	I	M

?What went wrong?

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Possibilities

- **Wrongly chosen active space (need to treat more than just on-site d-d interactions dynamically)**
- **Wrong embedding (double counting)**
- **Wrong approximation (need more than single-site DMFT)**
- **Wrong treatment of "background" electrons**

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Our view now

- **Pseudo cubic materials: the problem is with the underlying band structure**

- **Cuprates: need to fix underlying band structure and go beyond single-site DMFT**

Crucial Importance of p-d energy splitting

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$SrVO_3$: an instructive example

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$SrVO_3$: an instructive example

Cubic, moderately correlated metal

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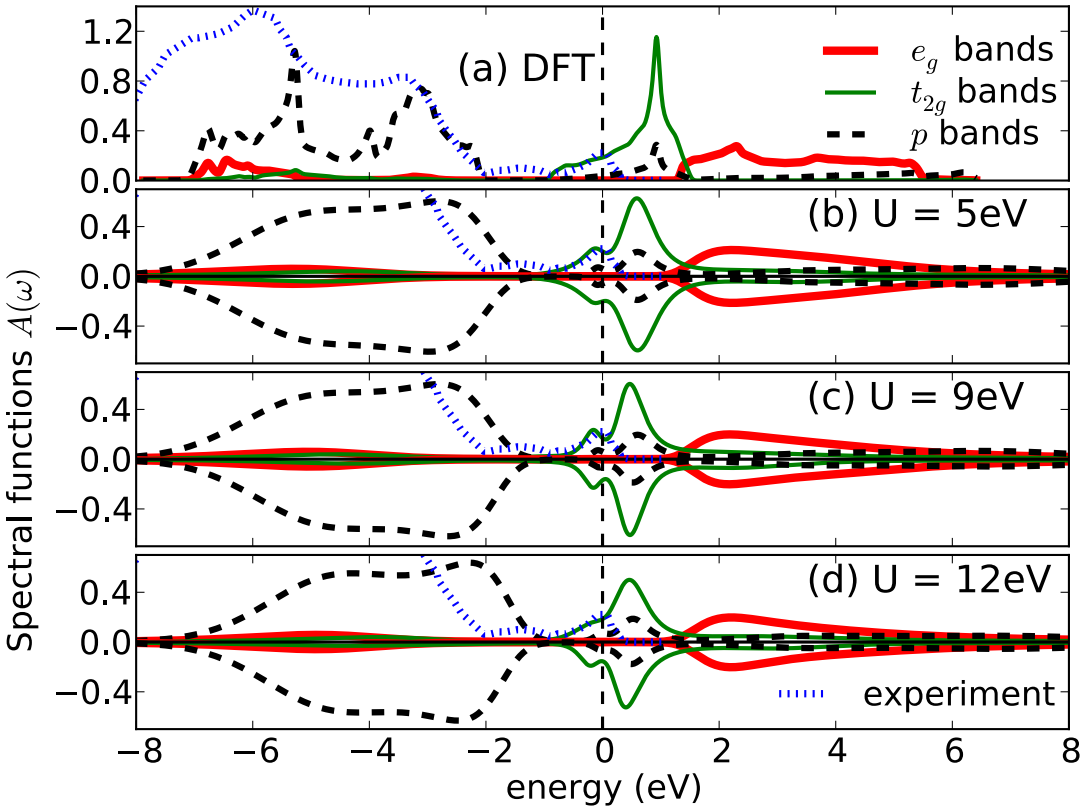
$SrVO_3$: an instructive example

Cubic, moderately correlated metal

DFT+DMFT TRIQS Code



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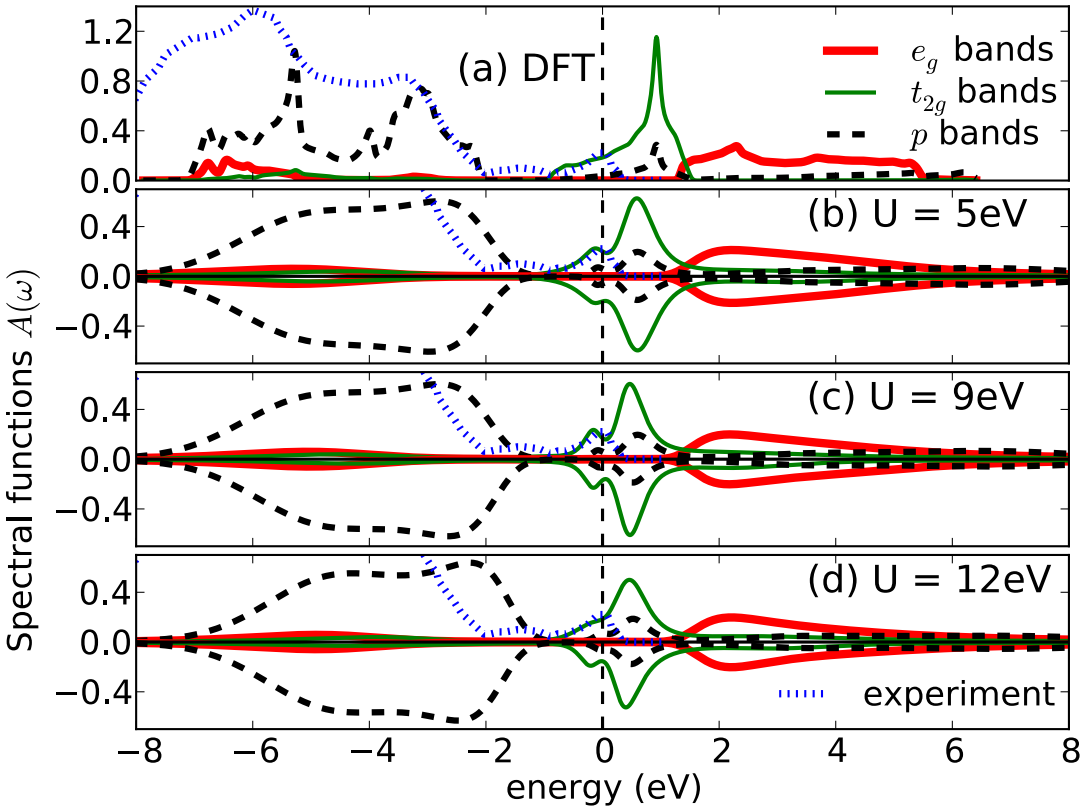
$SrVO_3$: an instructive example

Cubic, moderately correlated metal

DFT+DMFT TRIQS Code



process keeps relative separation of p and d bands independent of U-- and slightly smaller than band theory value

Without charge self consistency, p-bands stay at DFT position

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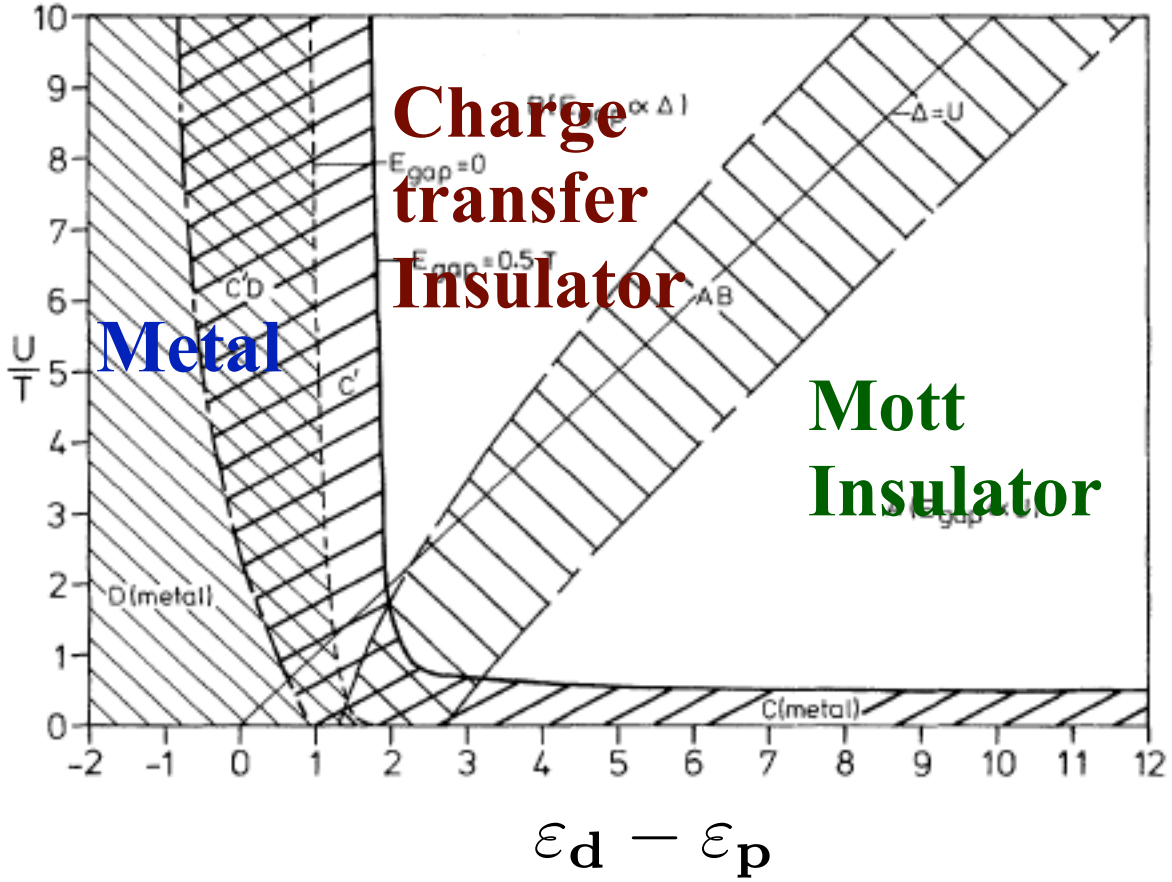
The Zaanen-Sawatzky-Allen phase diagram (integer band filling)



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Band Gaps and Electronic Structure of Transition-Metal Compounds

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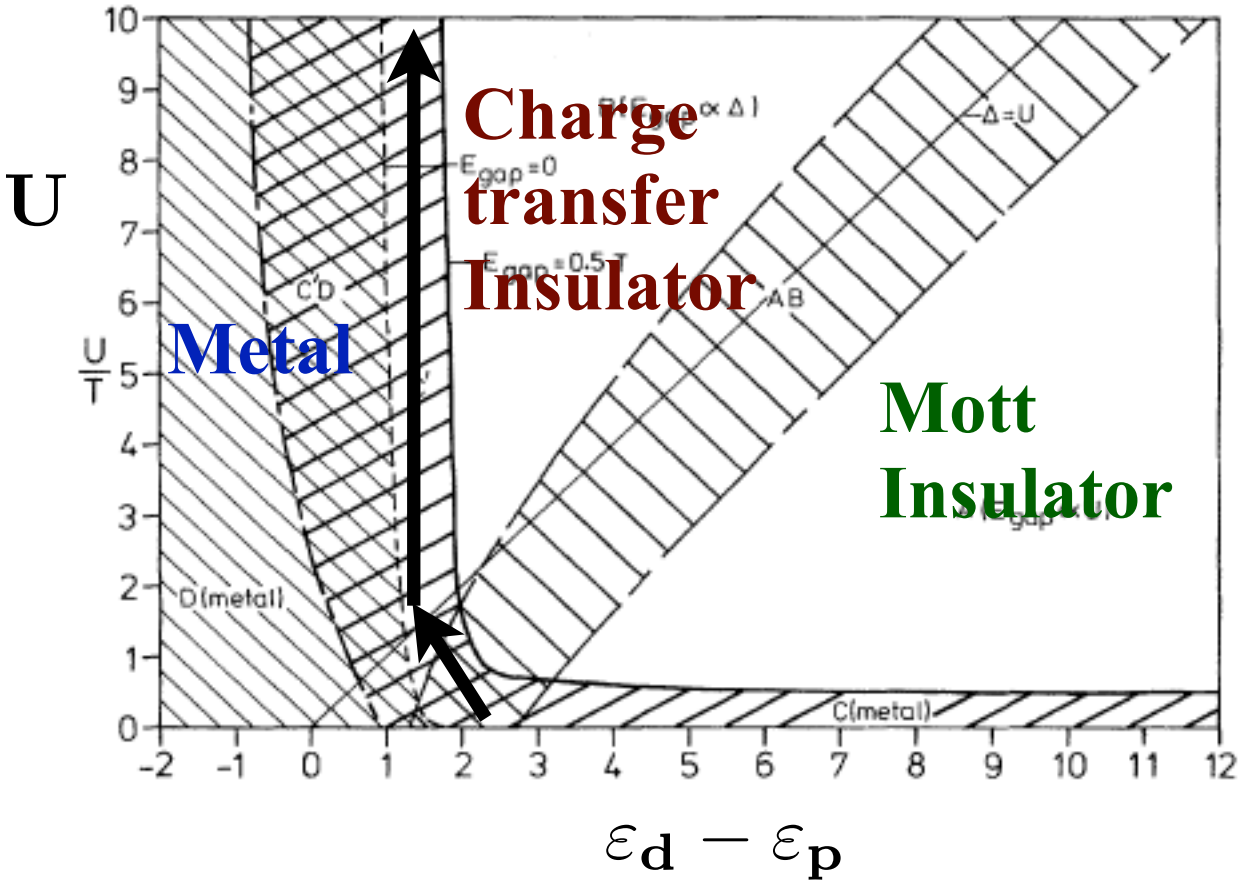
Calculation says that increasing U moves you more or less vertically in the ZSA phase diagram.



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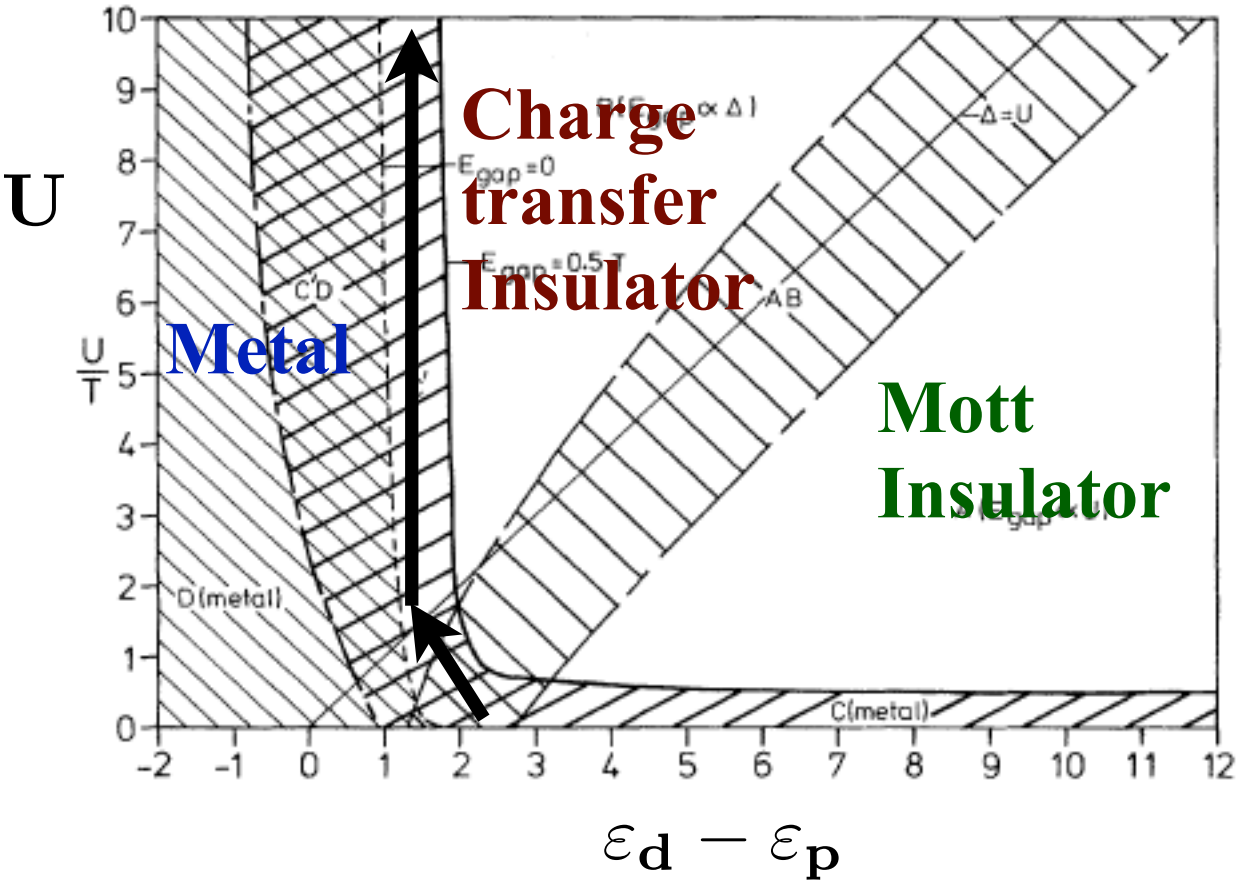
Calculation says that increasing U moves you more or less vertically in the ZSA phase diagram.



If the material starts with too small a p-d energy splitting, it remains in the metallic regime as U increases

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Would like to explore all of ZSa phase diagram

Fully charge self consistent calculation explores only one line.

?how to generalize?

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d-occupancy:

* Intuitive notion: e.g. $La^{3+}Ti^{3+}O_3^{2-}$ =>Ti d^1 (N_d=1)

*Theoretically needed (if you want to put correlations on d-orbital you need to know what this orbital is and how much it is occupied)

*definition:

In terms of exact Green function $\mathbf{G}(\mathbf{r},\mathbf{r}';\omega)$
and predefined d-wave function $\phi_{\mathbf{d}}$

$$\mathbf{N_d} = \sum_{\mathbf{a},\sigma} \int \frac{\mathbf{d}\omega}{\pi} \mathbf{f}(\omega) \int \mathbf{d^3 r d^3 r'}\ \mathbf{Im}\left[(\phi^{\mathbf{a}}_{\mathbf{d}}(\mathbf{r}))^* \, \mathbf{G}_\sigma(\mathbf{r},\mathbf{r}',\omega) \phi^{\mathbf{a}}_{\mathbf{d}}(\mathbf{r}') \right]$$

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Notes

***d occupancy depends on how orbital is defined (as does the entire edifice of DFT+DMFT)**

We have found: all reasonable definitions give consistent answers

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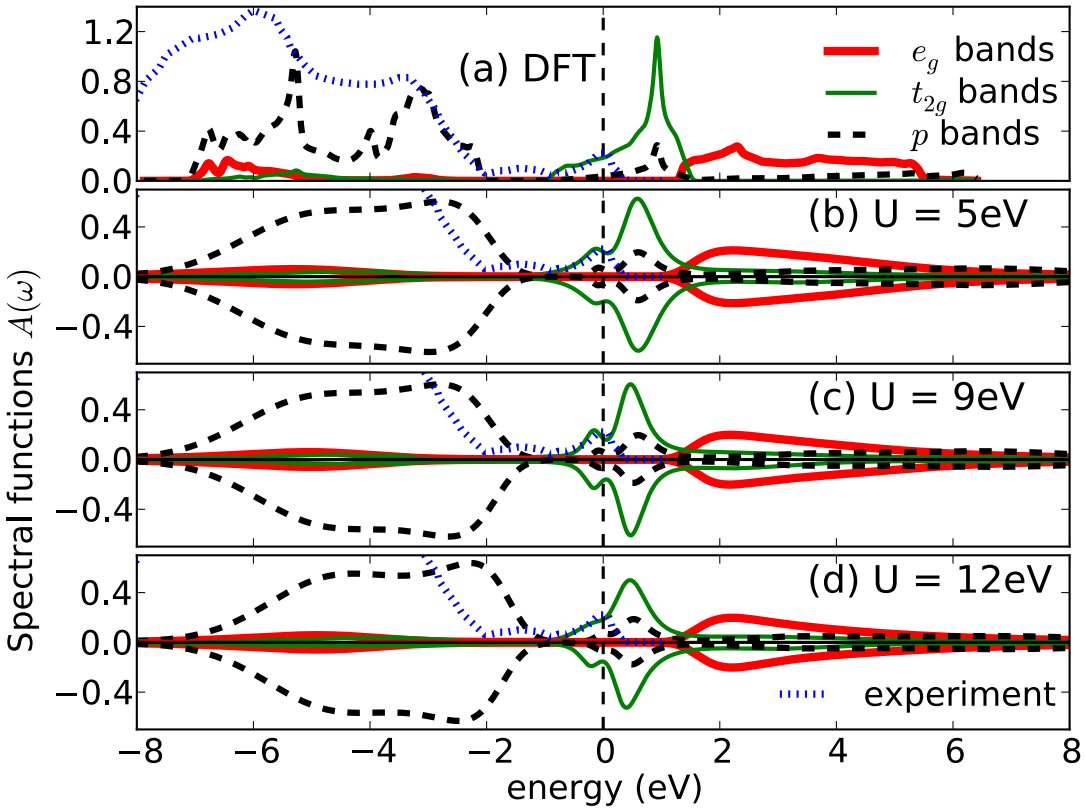
$SrVO_3$:

DFT+DMFT TRIQS Code



lower panels: ad-hoc double counting correction chosen to keep N_d at value found in fully charge self consistent calculation.

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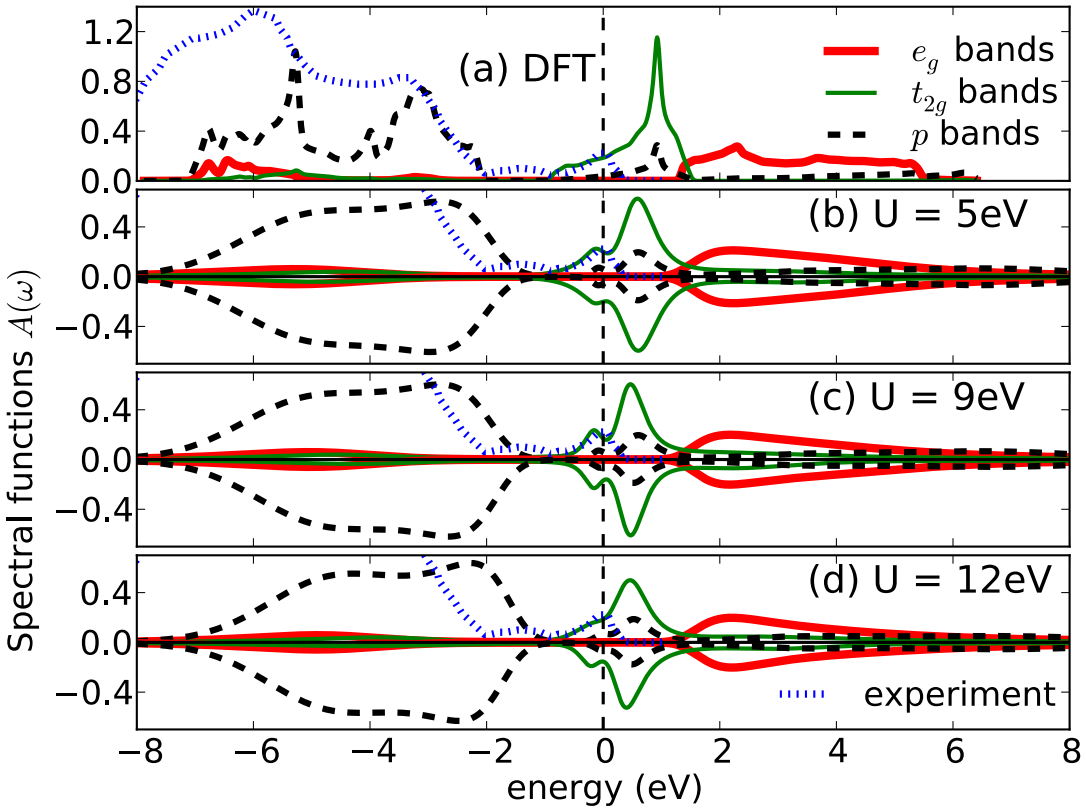
$SrVO_3$:

DFT+DMFT TRIQS Code



lower panels: ad-hoc double counting correction chosen to keep N_d at value found in fully charge self consistent calculation.

Spectra are identical.

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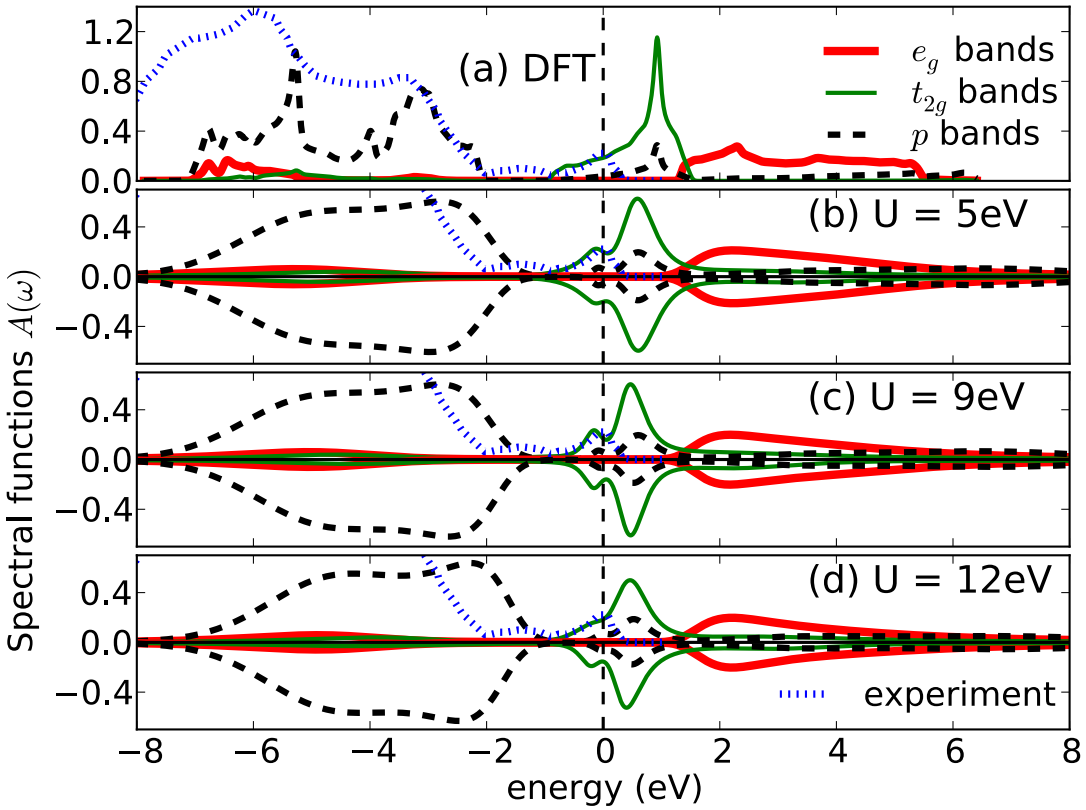
$SrVO_3$:

DFT+DMFT TRIQS Code



lower panels: ad-hoc double counting correction chosen to keep N_d at value found in fully charge self consistent calculation.

Spectra are identical.

=>dont need to bother with charge self consistency; plot results in terms of N_d

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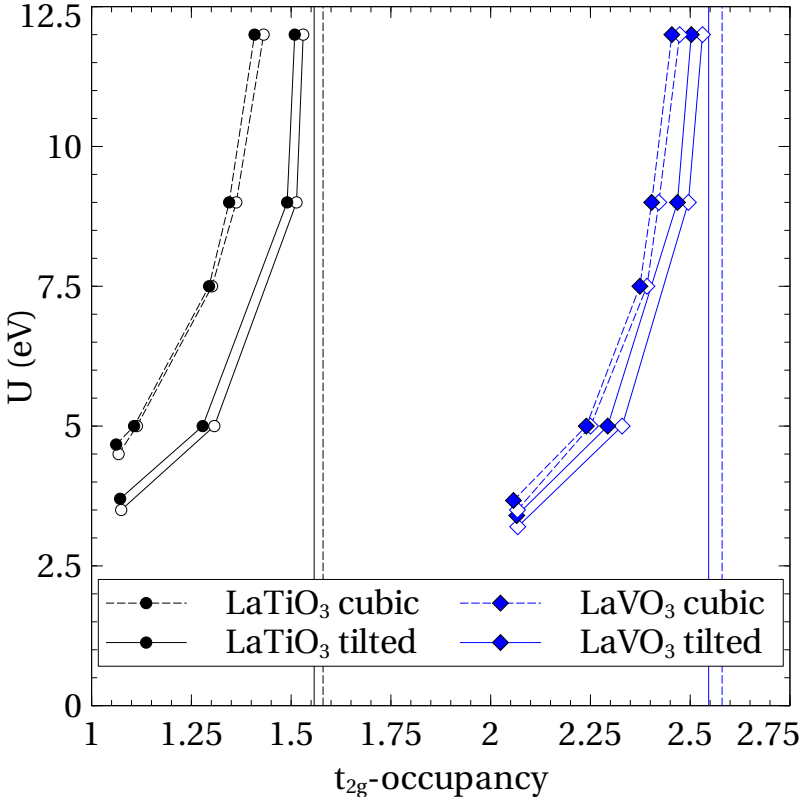
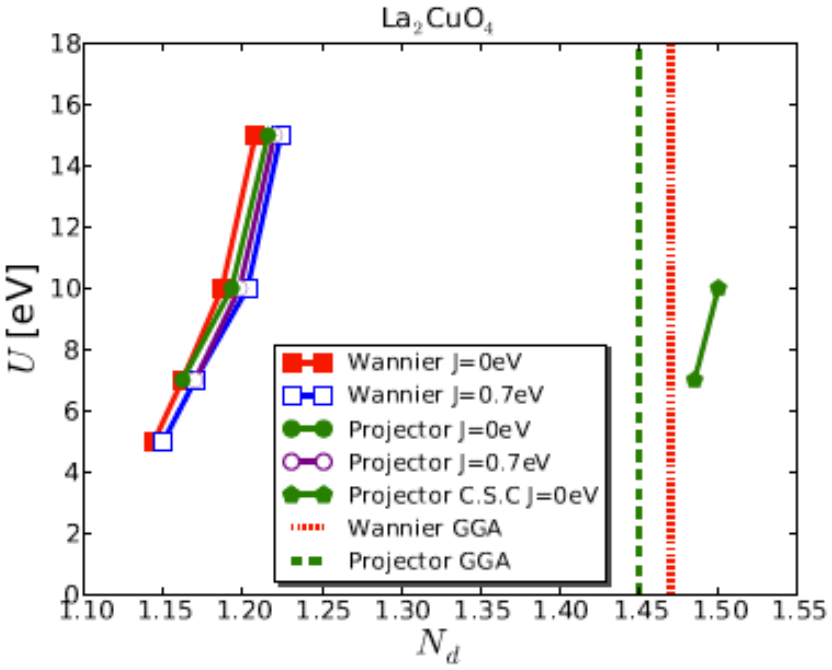
Metal-insulator phase diagrams





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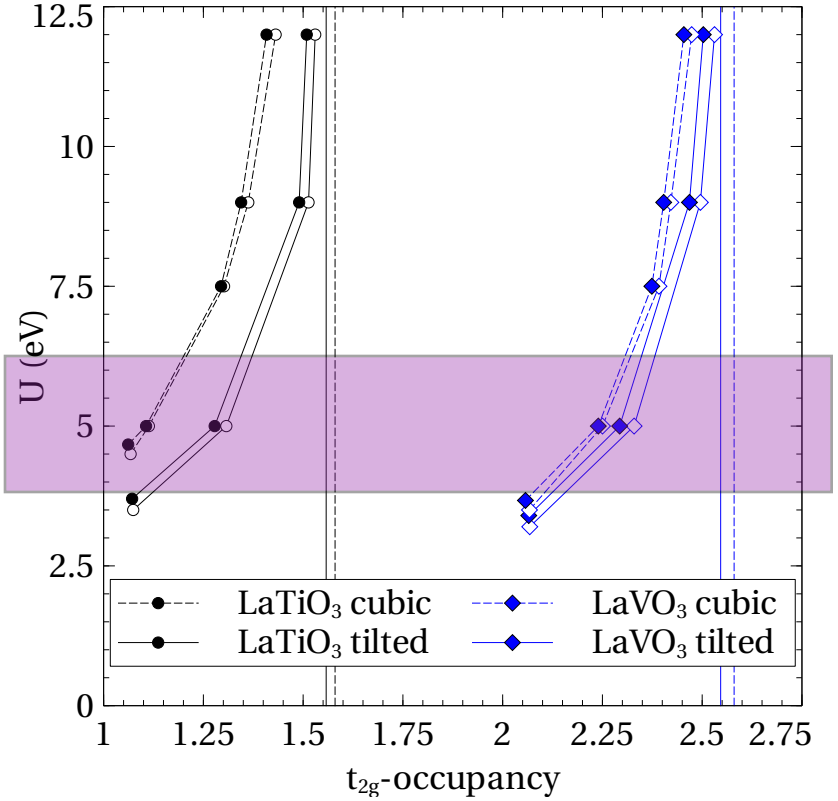
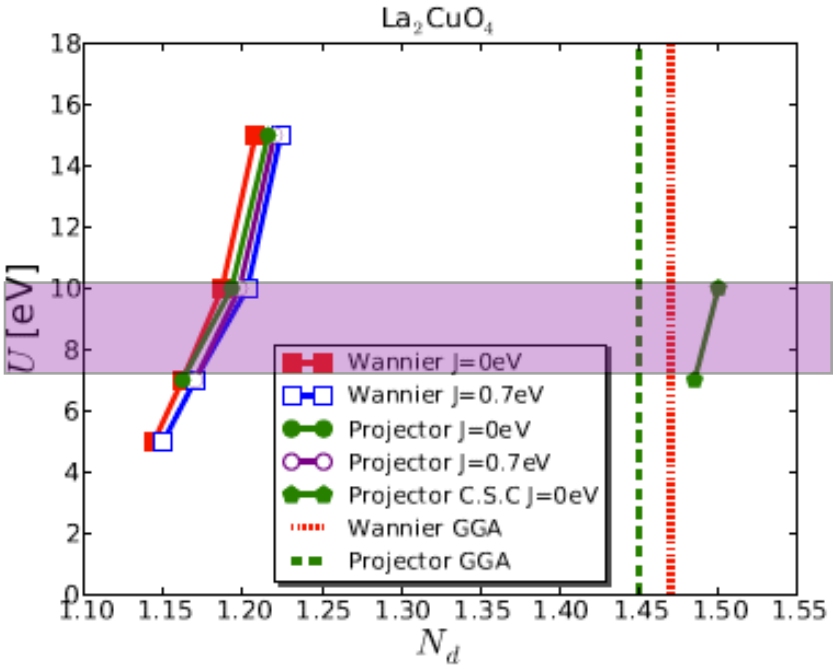
Metal-insulator phase diagrams





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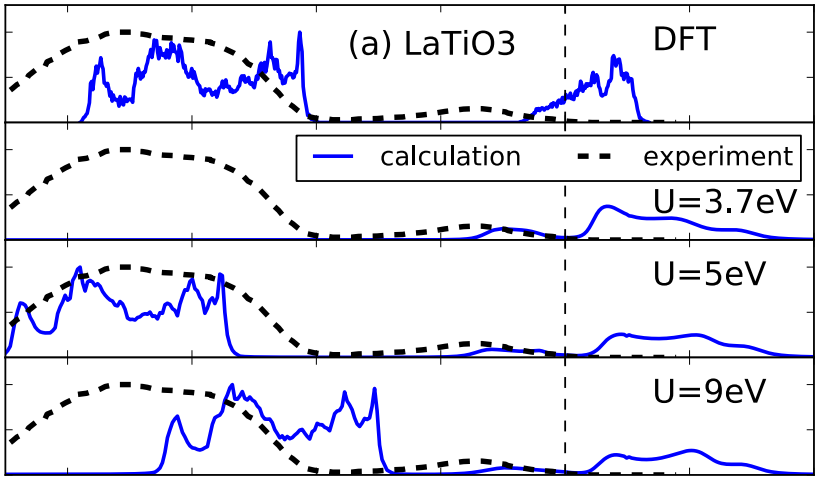
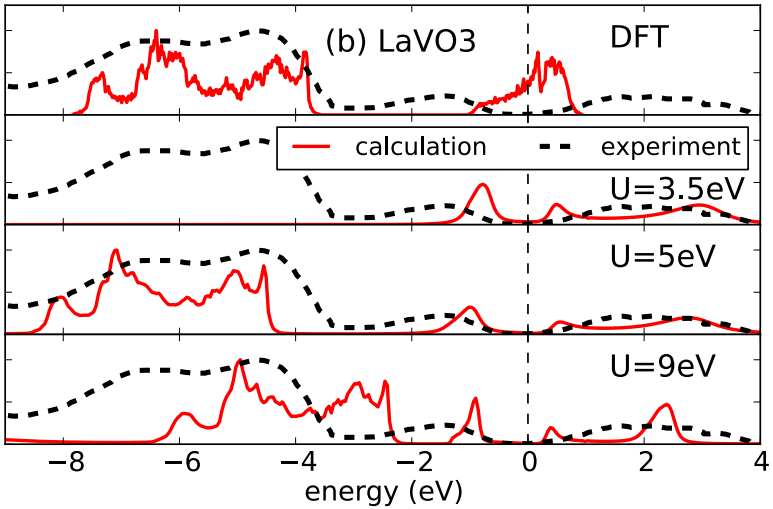
Titanates/Vanadates

For each U, adjust Nd so theory gives insulating gap in agreement with experiment. Compute oxygen bands.





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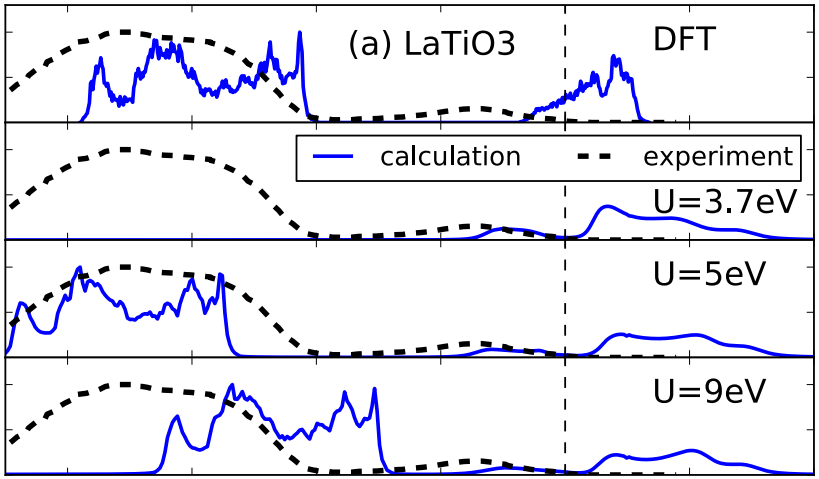
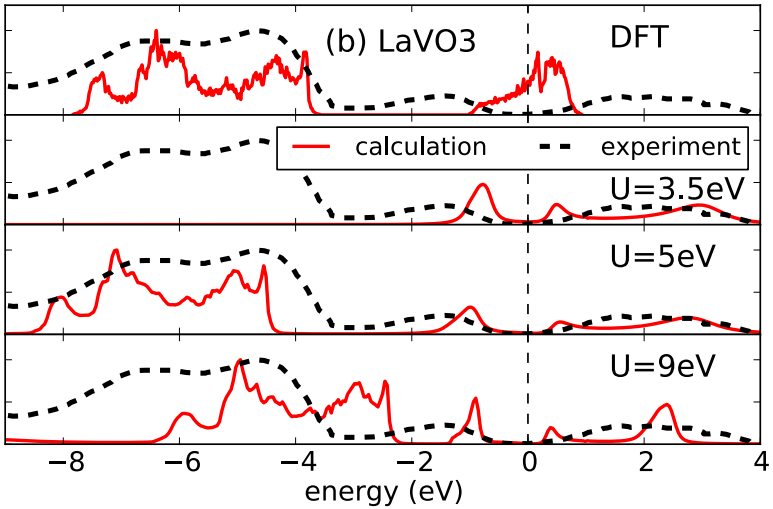
Titanates/Vanadates

For each U, adjust Nd so theory gives insulating gap in agreement with experiment. Compute oxygen bands.

Relatively narrow U-range consistent with expt





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Titanates/Vanadates

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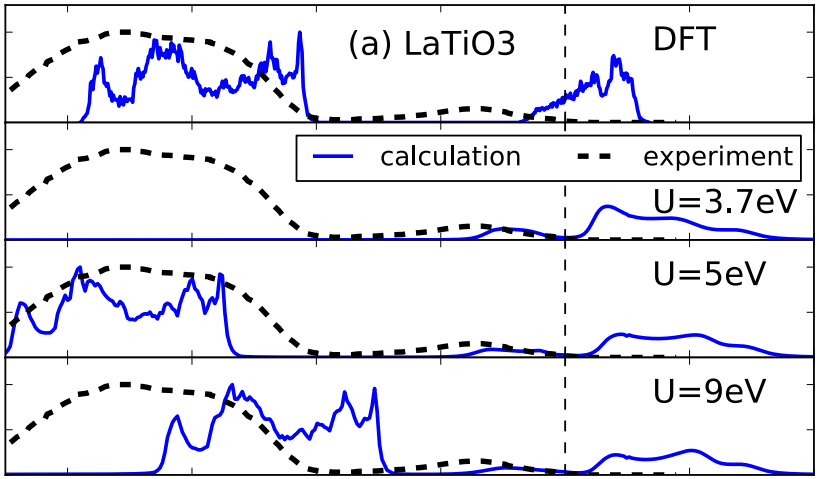

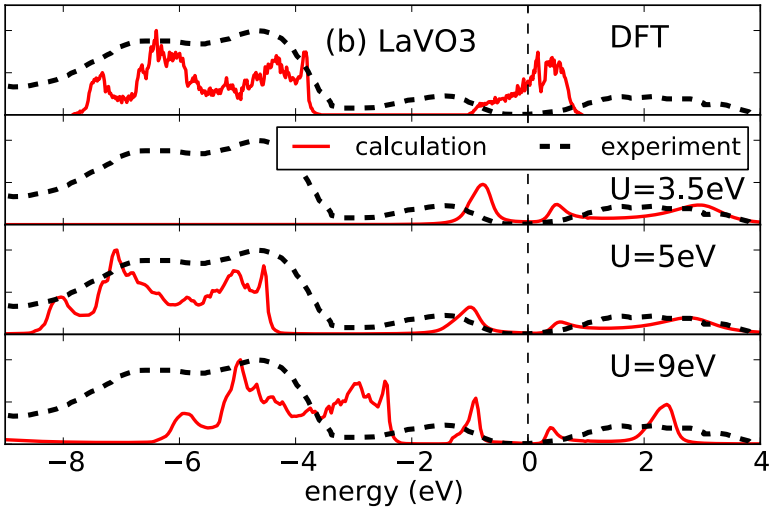

U~5-6eV is found in C-RPA calculations

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Possibilities

- **Wrongly chosen active space (need to treat more than just on-site d-d interactions dynamically)**
- **Wrong embedding (double counting)**
- **Wrong approximation (need more than single-site DMFT)**
- **Wrong treatment of "background" electrons**

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Summary: titanates/vanadates

Single-site DMFT is acceptable first-order approximation to electronic structure **IF oxygen bands are suitably positioned**

Fully charge self consistent DFT+DMFT places oxygen bands higher than DFT and thus too high relative to experiment.

=>?need better background electronic structure?

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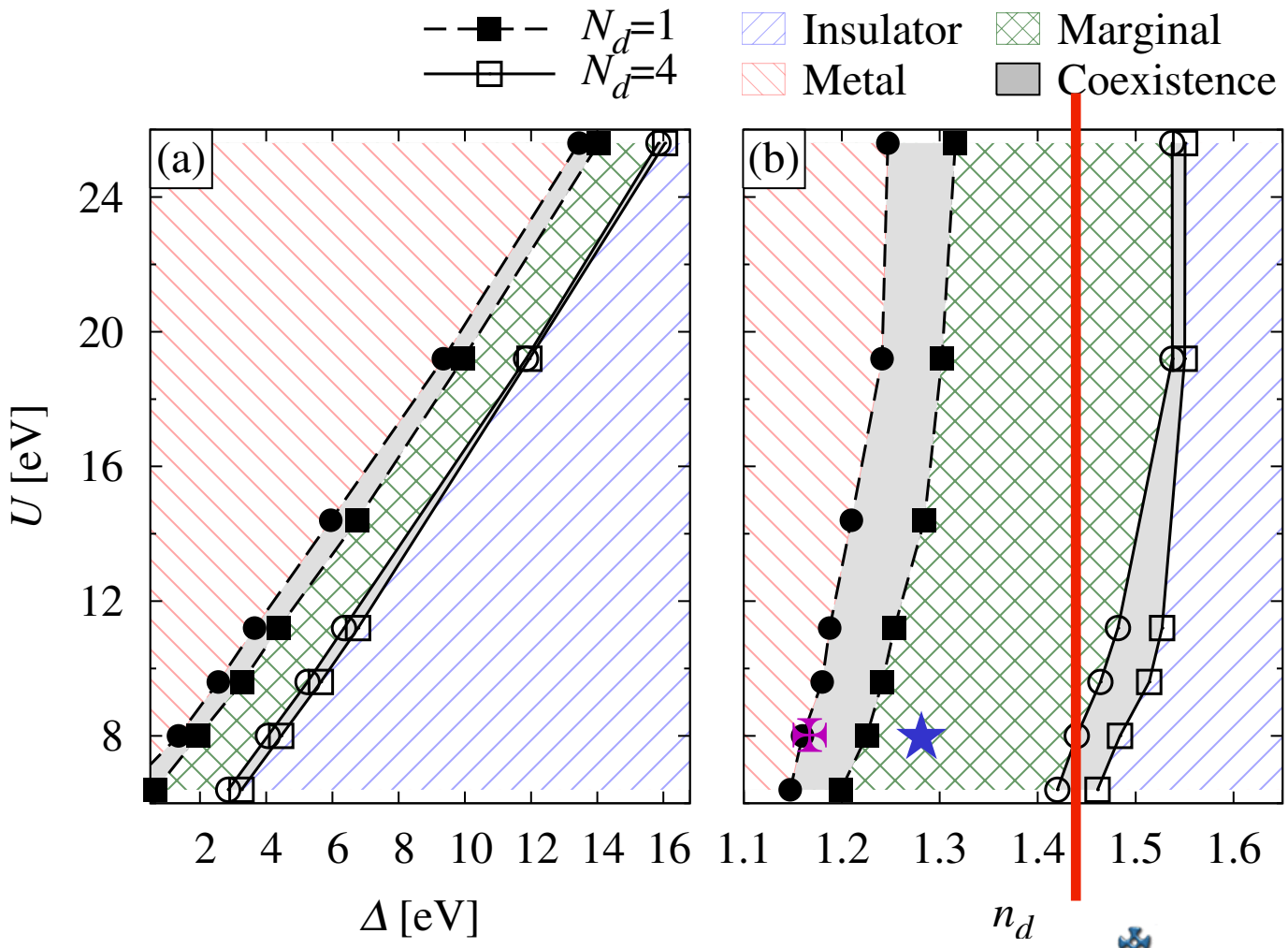
Cuprates: beyond single-site dmft

Ara Go. (New CI-based ``impurity solver")



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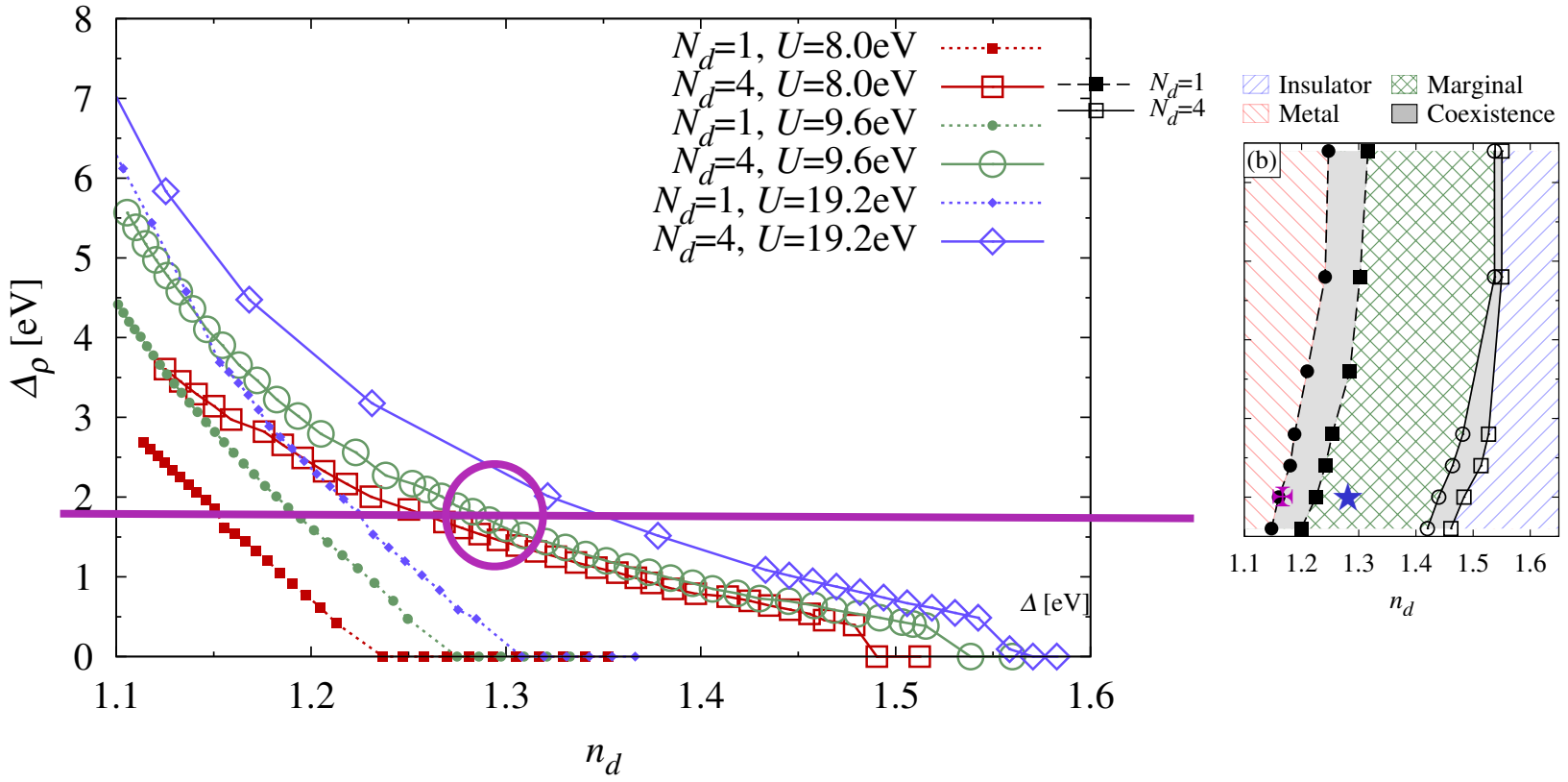
Gap



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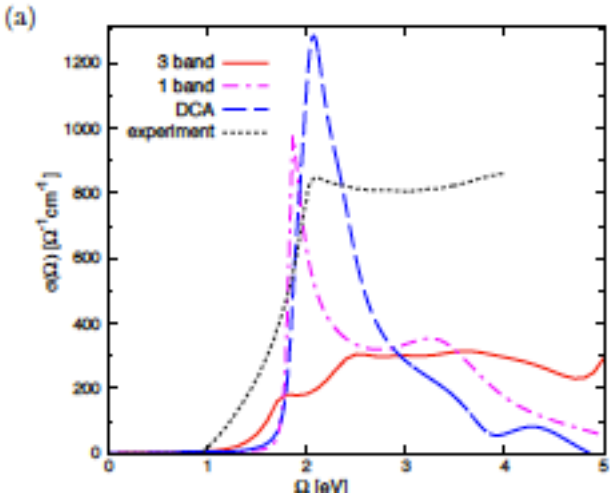
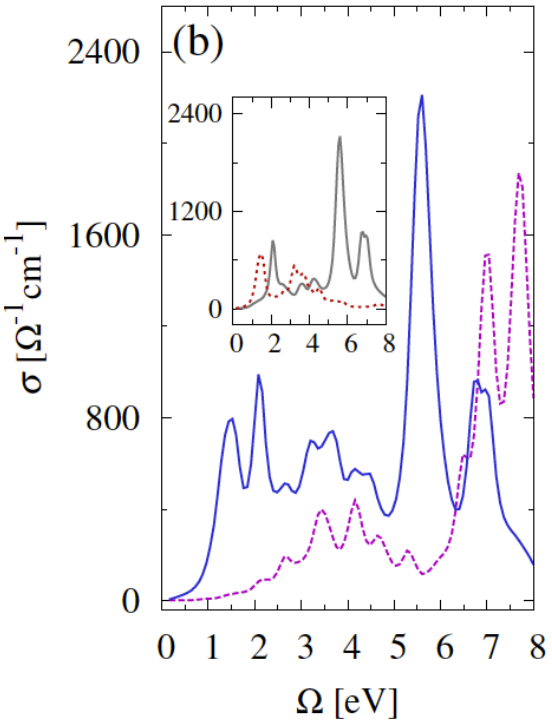
Resolves old problem in optics

Xin Wang
2011



Ara Go: 2013



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Summary: cuprates

4-site DMFT is acceptable first-order approximation to electronic structure **IF oxygen bands are suitably positioned**

Long-standing problem with optics resolved

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Very recent success: energetics of nontrivial phases

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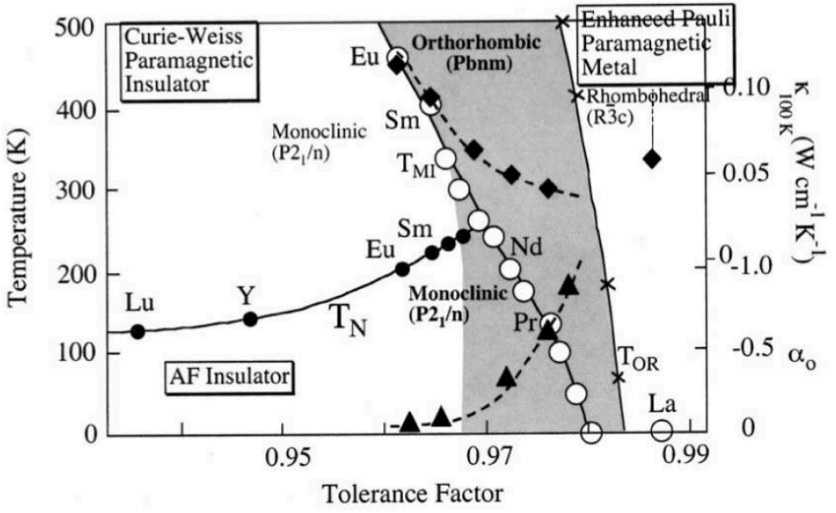
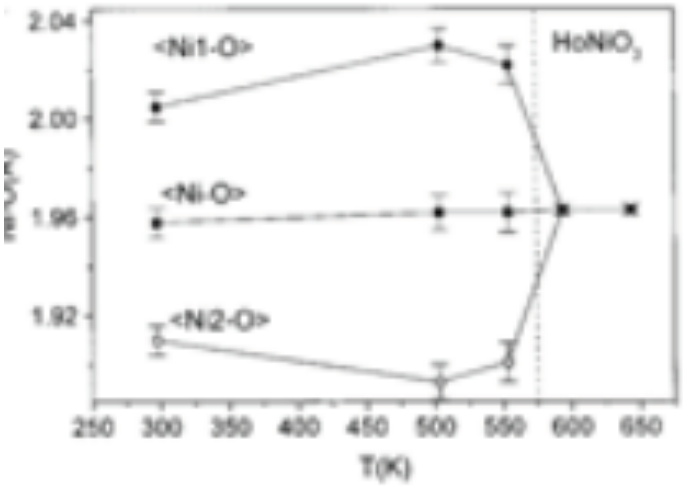
metal-insulator transition in rare-earth nickel oxides





J A Alonso et al PRL 82 3871 (1999)

Metal-insulator transition occurs along with 2 sublattice Ni-O breathing distortion

Wrongly interpreted as charge order

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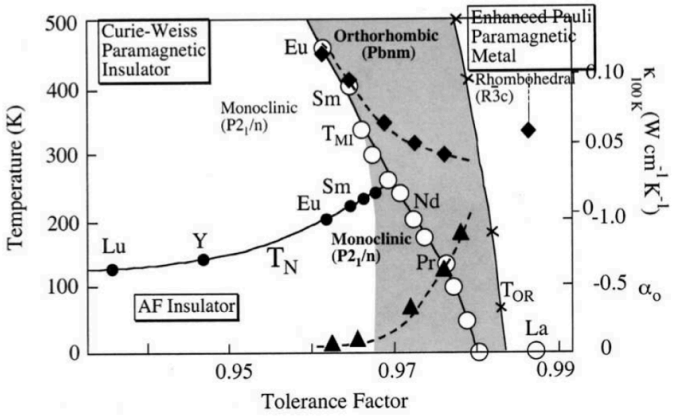
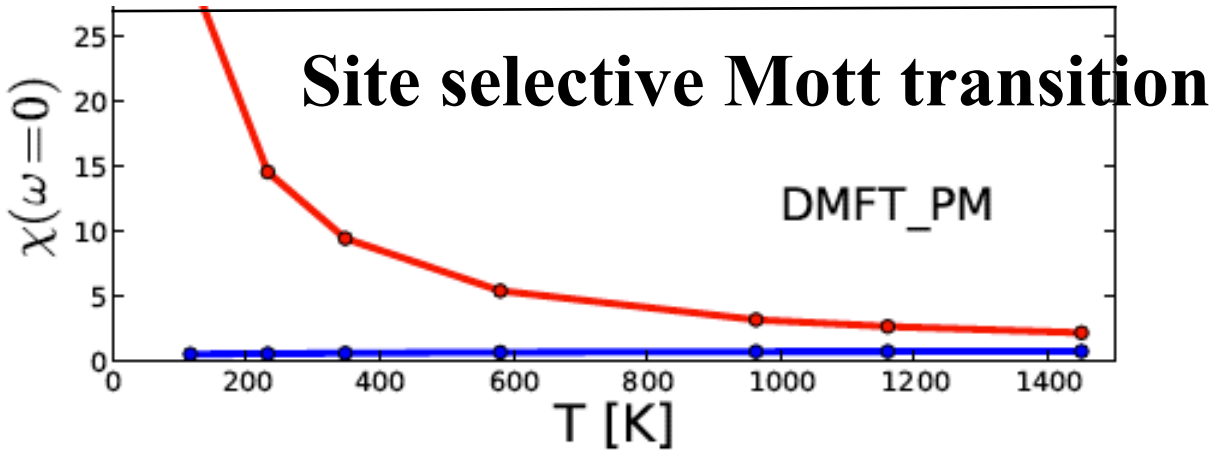
DFT+DMFT using observed structure of insulating phase



Find: insulator but no charge order

N_1=8.24 N_2=8.22



Hyowon Park, Andrew J. Millis, and Chris A. Marianetti, PRL 109, 156402 (2012)

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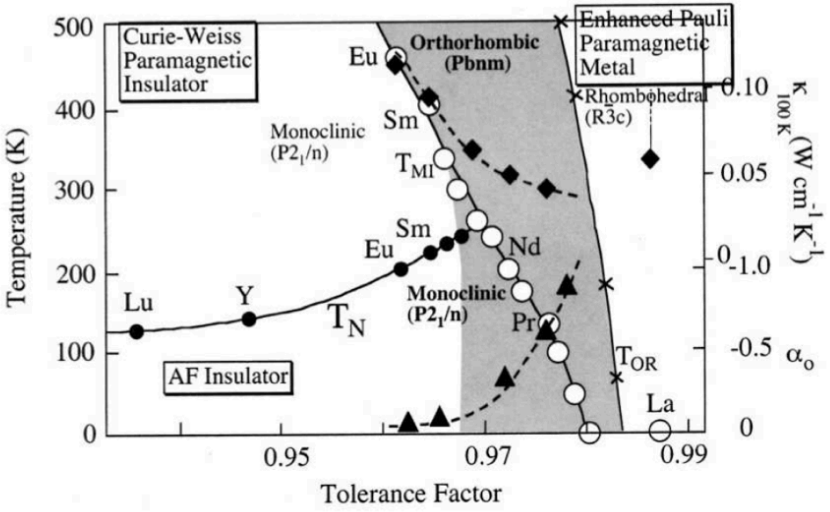
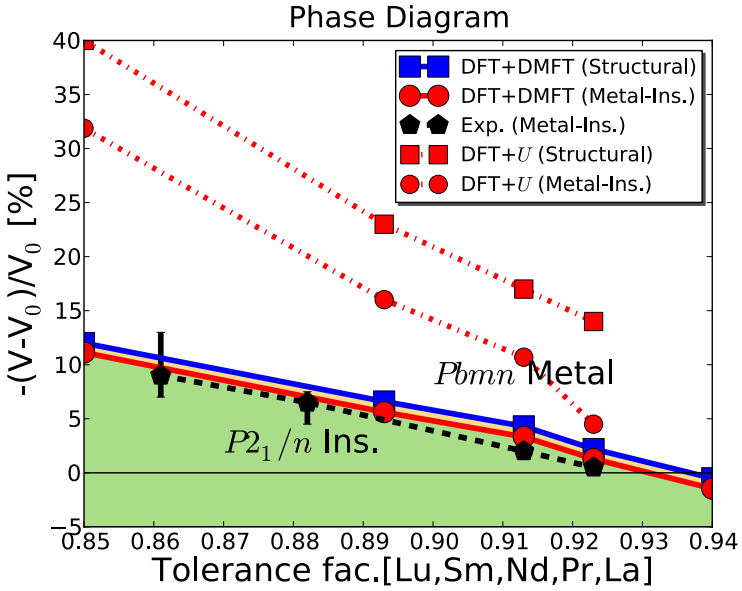
Can now compute energies and pressure-volume phase diagrams





Hyowon Park, Andrew J. Millis, and Chris A. Marianetti, to appear

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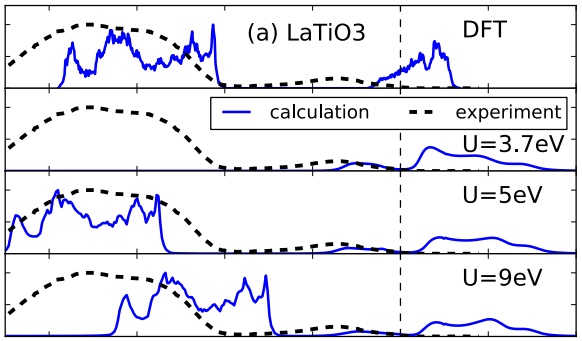
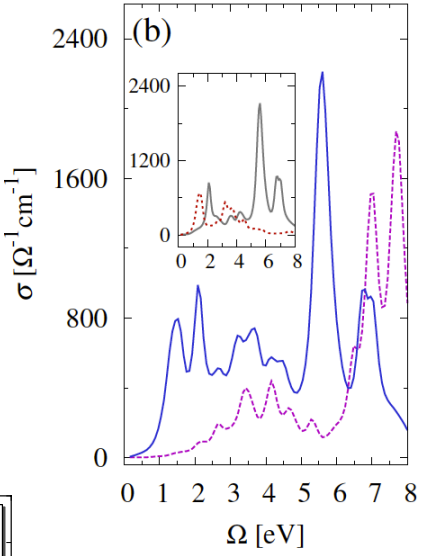
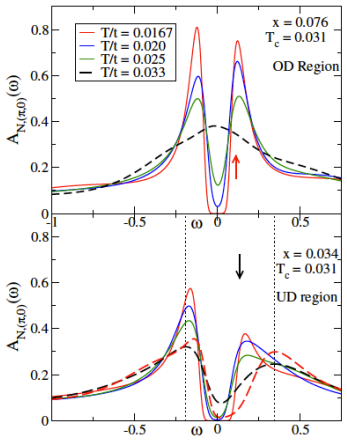
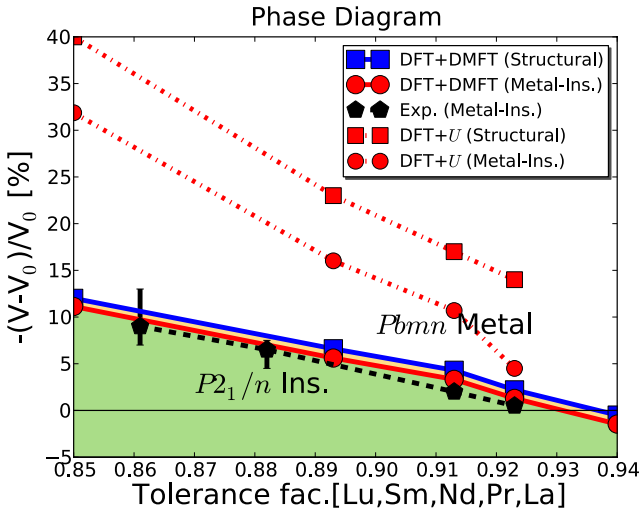
Conclusion









Conclusion: need underlying electronic structure that gets the oxygen energies right. DFt puts O states too close to the fermi level

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Prospects: DFT+DMFT

1. background electronic structure
   1.1. beyond DFT method
2. Active subspace: ?atomic-like d-orbitals?
3. ?On-site intra-d interactions?
4. Solve active space (?DMFT?)
   4.1. if only on-site interactions
   4.2. is single-site approx ok?
5. Embed

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Cuprates

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Cuprates

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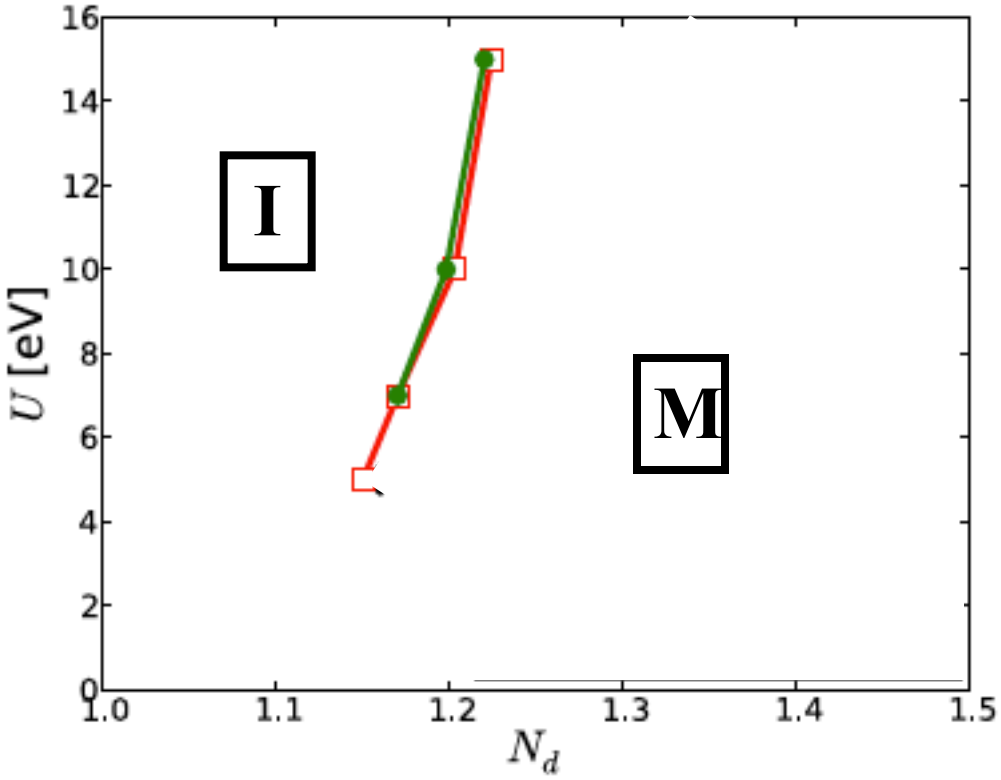
U-Nd phase diagram

DFT+DMFT: treat only Cu-d x^2-y^2 orbital dynamically



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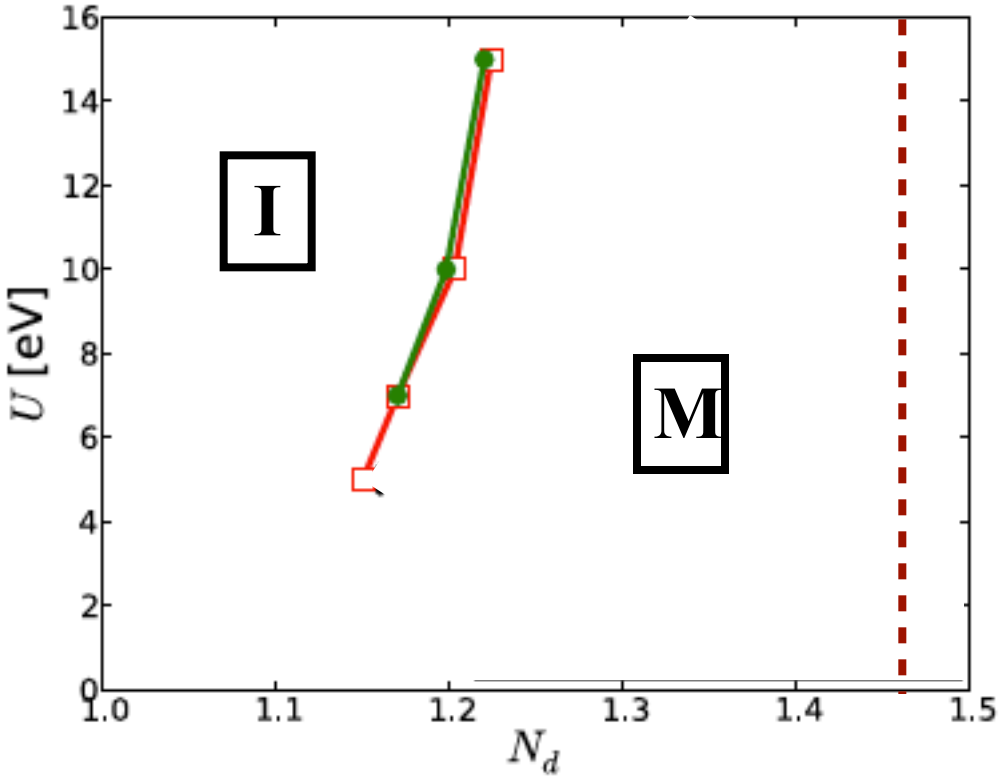
U-Nd phase diagram

DFT+DMFT: treat only Cu-d x^2-y^2 orbital dynamically

band theory



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U-Nd phase diagram

DFT+DMFT: treat only Cu-d x^2-y^2 orbital dynamically

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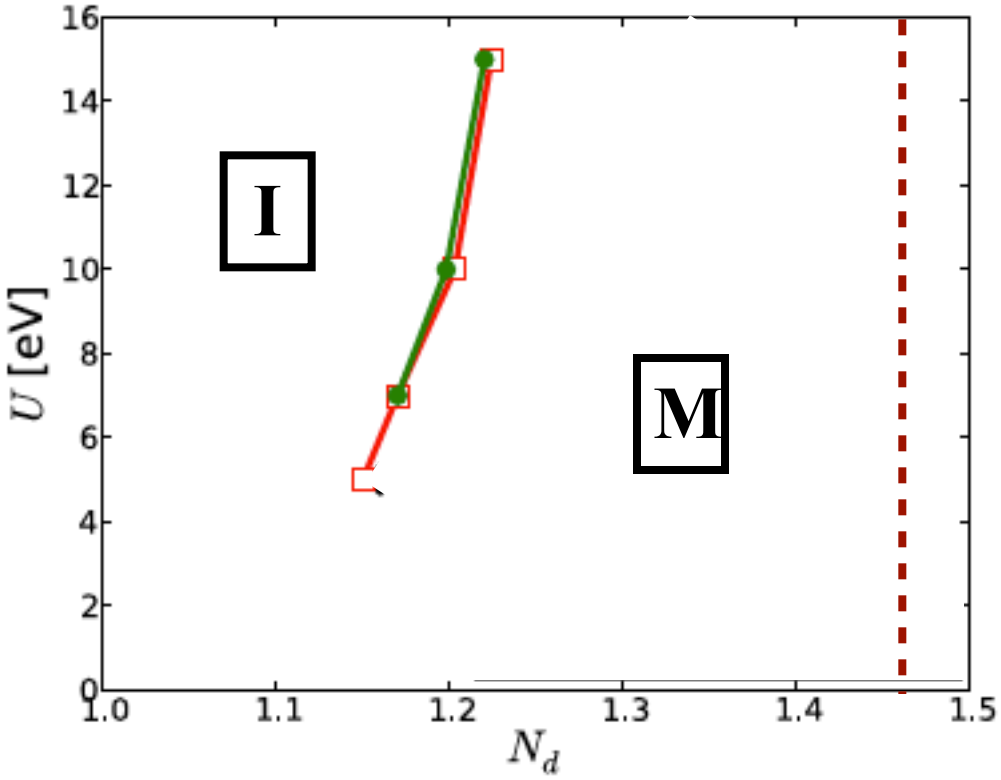

'distance' from band theory Nd to metal-insulator phase boundary ~0.25el/Cu

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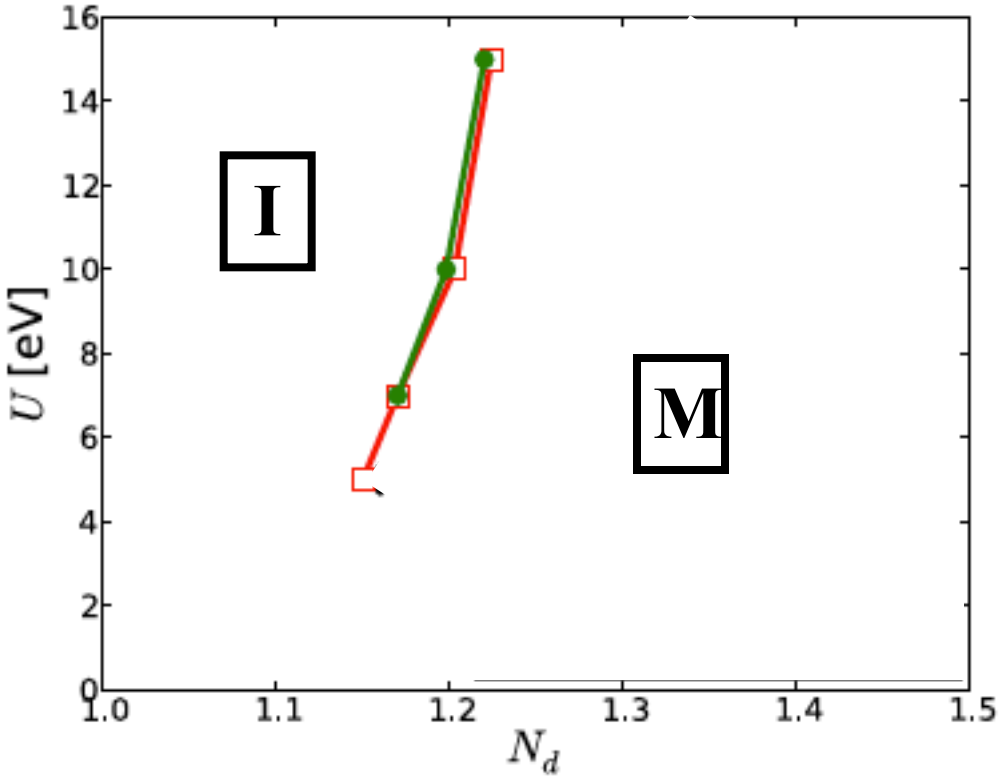
U-Nd phase diagram

DFT+DMFT: treat Cu-d x^2-y^2 orbital dynamically
Non-self-consistent



VASP/MLWF
Wein2K/Projector

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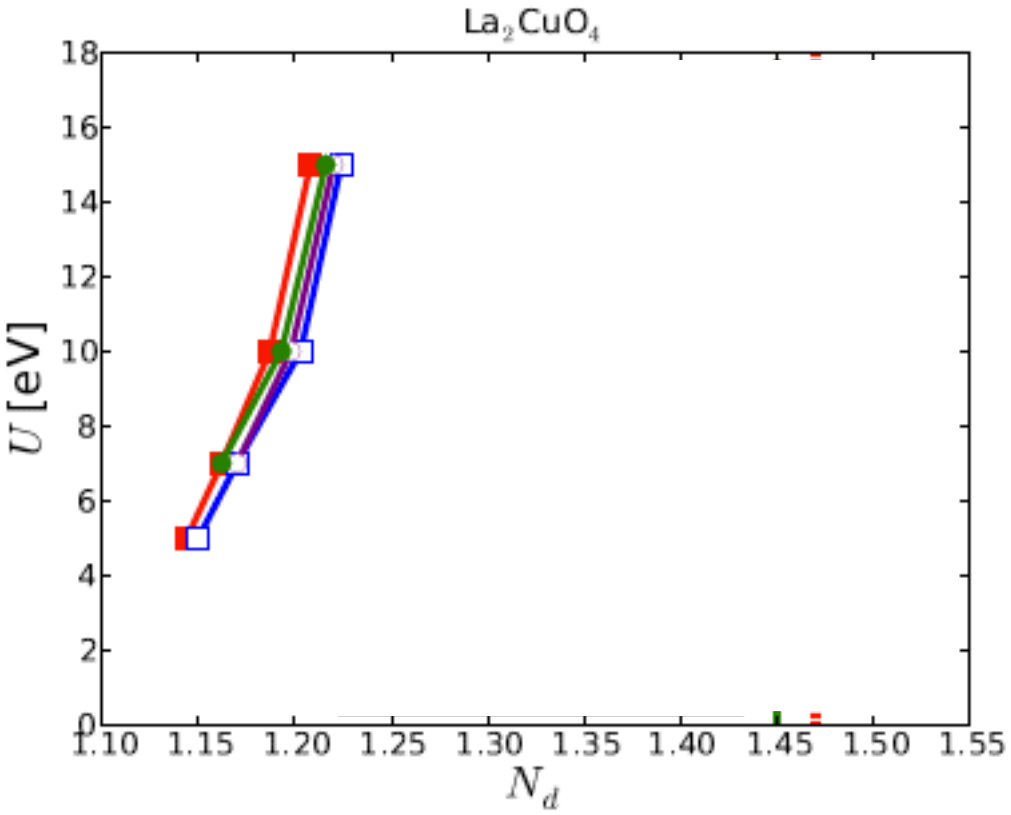
More detailed look



Treat x2-y2 dynamically, all other d with Hartree-Fock J=0 vs J=0.7eV

vs

treat all 5 d dynamically (only Ising terms) J=0 vs J=0.7eV

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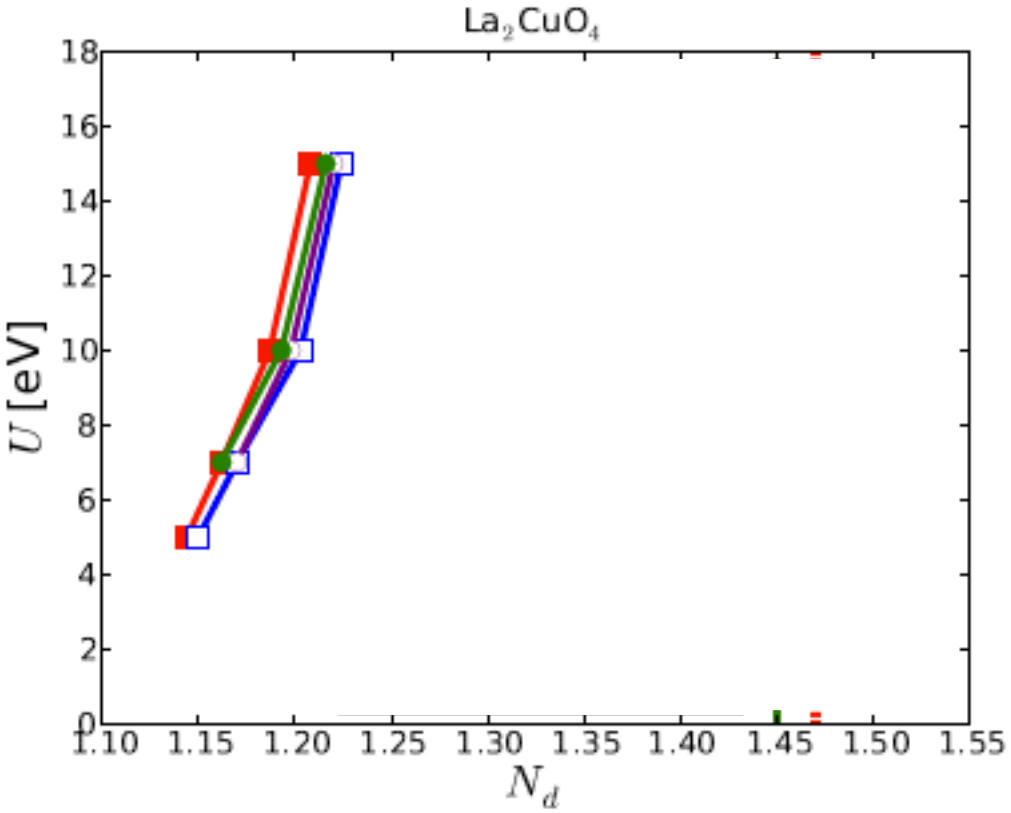
What is band theory N_d?



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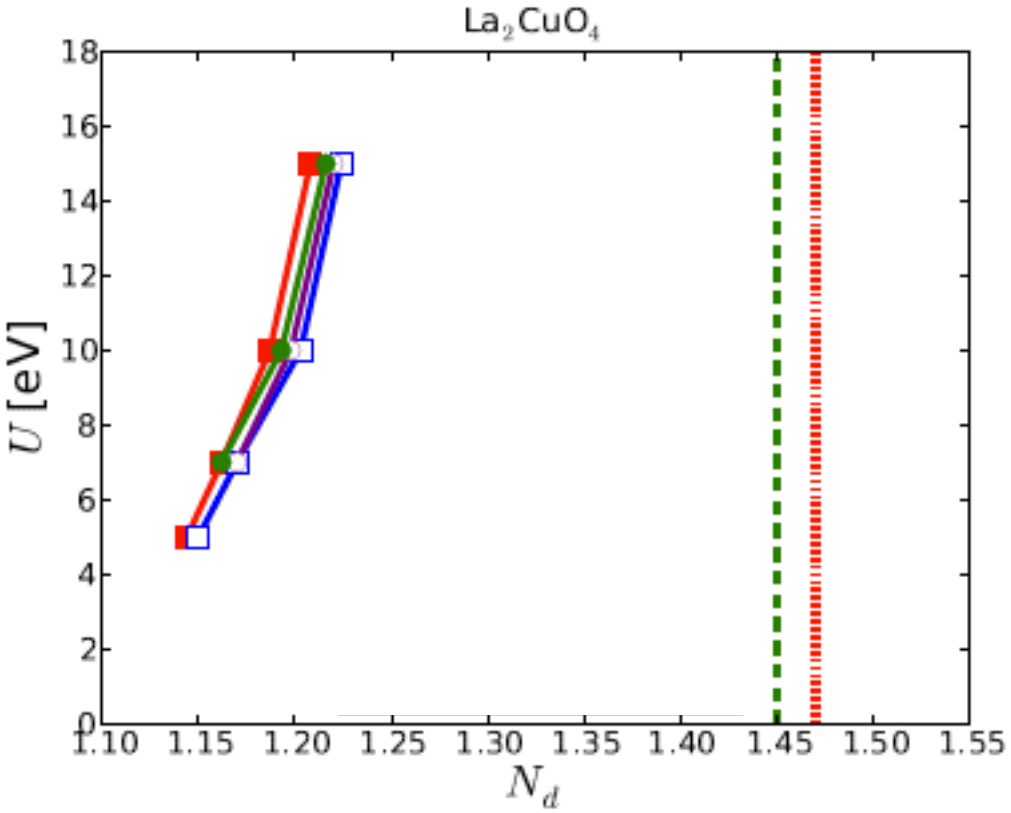

VASP/Wannier

Wein2K/projector

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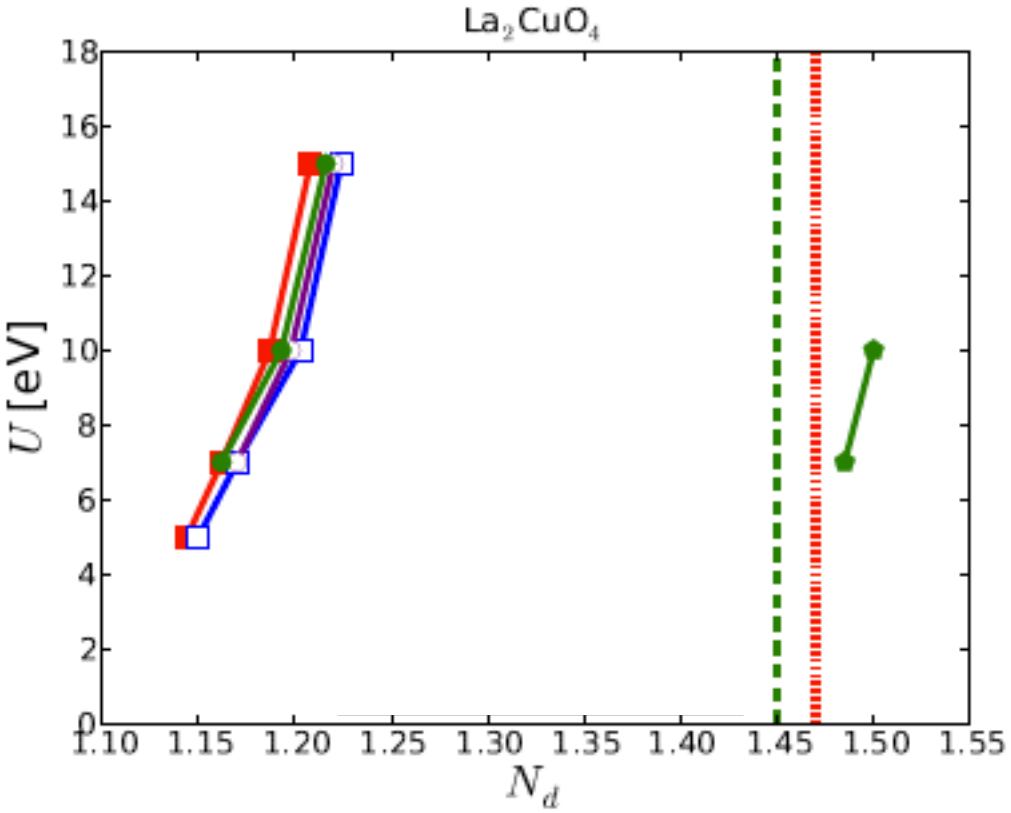
What about full charge self-consistency



Wein2K/projector

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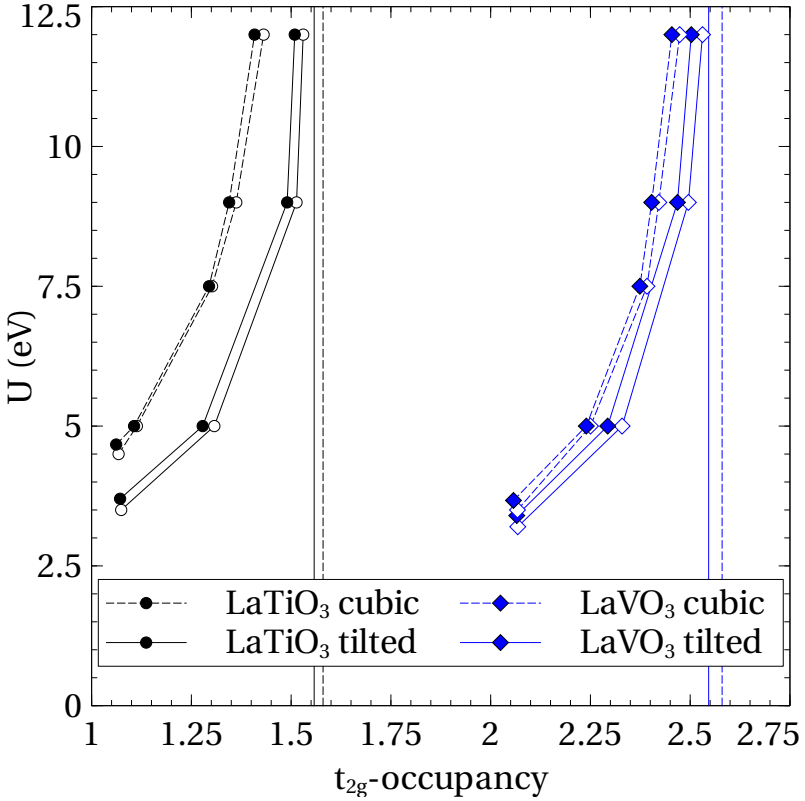
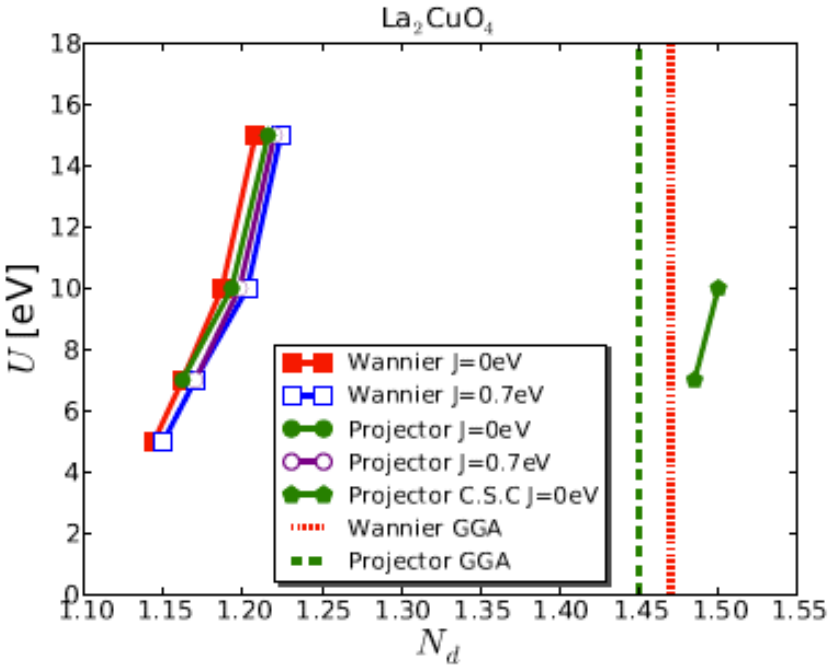
Metal-insulator phase diagrams





?How to position the materials?

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