

# **Numerical Methods for Correlated Electron Systems**

**A. J. Millis**

**Department of Physics, Columbia University  
and  
The Simons Foundation**

**Support: DOE ER-046169 and NSF DMR 13086282**

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# The Flatiron Institute of the Simons Foundation

**Mission: computationally oriented research in the physical and life sciences**

**When fully established:**

- 250 staff members
- 4 scientific units
- +computational core
- Now open for business
  - CCA (Astronomy) 2016
  - CCB (Life Sciences) 2015
  - and...



CENTER MODULE  
COMMONS - LOWER FLOOR



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# Center for Computational Quantum Physics (CCQ)

**Director:**  
**Antoine Georges**

Antoine Georges to Lead New Center for Computational Quantum Physics

January 6, 2017

The Simons Foundation is delighted to announce the formation of the Center for Computational Quantum Physics (CCQ), in the foundation's new Watson Institute, and the appointment of Antoine Georges as its director.

A new era is dawning in our ability to understand and control the behavior of materials and molecules. The CCQ will develop the concepts, algorithms and computational tools needed to handle many-body quantum systems and capture the quantum dynamics of electrons and ions in chemically realistic environments and make them available to the scientific community. The center will also host a lively array of meetings, workshops and conferences, serving as a focal point for computational materials science internationally. At full strength, the center is expected to comprise up to 60 scientific and support personnel, including both junior and senior positions, as well as sabbatical and summer visitors.



Antoine Georges

Antoine Georges holds the chair in condensed matter physics at the Collège de France and is also professor of physics at Ecole Polytechnique and at the University of Geneva. His work has been recognized by numerous fellowships and awards, including the Anatole and Suzanne Abregam Prize of the French Academy of Sciences, the 2004 Prix Dangeles, the 2006 Condensed Matter Europhysics Prize, the 2007 Médaille d'Argent of the CNRS, a 2012 Synergy award from the European Research Council and the 2014 Hamburg Prize for Theoretical Physics. He is a member of the French Academy of Sciences.

Andrew Mills, professor of physics at Columbia University, will serve as co-director of the CCQ.

**co-Director: AJM**

**Mission: concepts, theory, algorithms, codes and comparison to experiment for chemistry, condensed matter physics, materials science....**

**Official Start: 9/1/2017**

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# CCQ is now recruiting postdocs

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**Look for Flatiron Research Fellow CCQ on**

**<https://simonsfoundation.wd1.myworkdayjobs.com/simonsfoundationcareers>**

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# Define “strong correlations”: electron propagation

## Electron Spectral function $A(k, \omega)$

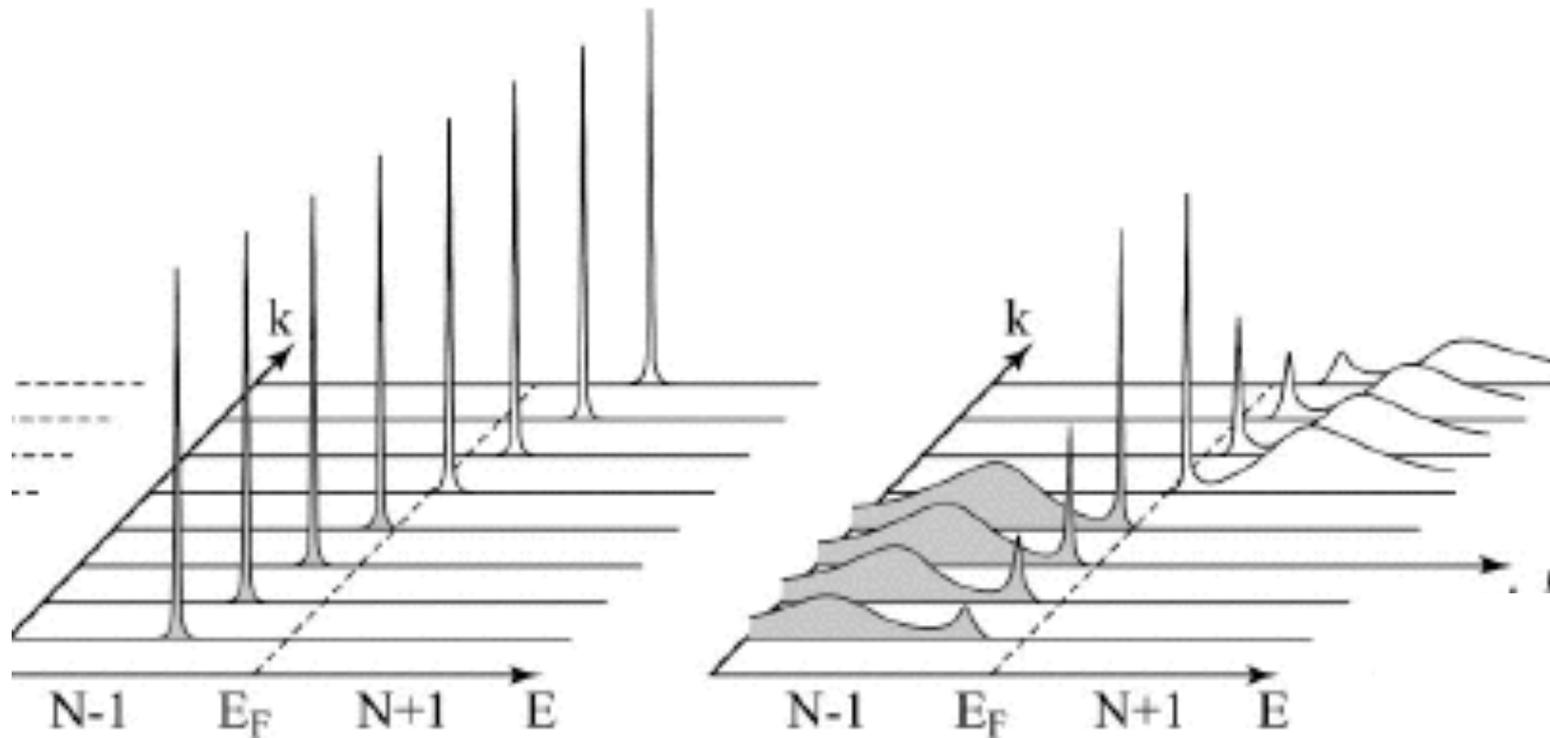


Fig. 3, Damascelli, Hussain and Shen RMP 75 473 (2003)

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# Alternative definition: wave function

$$\begin{aligned} \mathbf{A}(k, \omega) &= \text{Im} [G^R(k, \omega)] \\ &= \sum_m \langle GS | \psi_k | \Psi_{N+1}^m \rangle \langle \Psi_{N+1}^m | \psi_k^\dagger | GS \rangle \delta(\omega - E_{N+1}^m) \\ &+ \sum_m \langle GS | \psi_k^\dagger | \Psi_{N-1}^m \rangle \langle \Psi_{N-1}^m | \psi_k | GS \rangle \delta(\omega - E_{N-1}^m) \end{aligned}$$

**If ground state is close to single Slater Determinant**

$$|GS\rangle = \text{Det} \begin{bmatrix} \phi_{k_1}(x_1) & \phi_{k_2}(x_1) & \phi_{k_3}(x_1) & \dots \\ \phi_{k_1}(x_2) & \phi_{k_2}(x_2) & \phi_{k_3}(x_2) & \dots \\ \phi_{k_1}(x_3) & \phi_{k_2}(x_3) & \phi_{k_3}(x_3) & \dots \\ \phi_{k_1}(x_4) & \phi_{k_2}(x_4) & \phi_{k_3}(x_4) & \dots \\ \dots & \dots & \dots & \dots \end{bmatrix}$$

**Spectral function is close to delta-function**

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**“Strong correlation”**



**Multireference**

$$|\text{GS}\rangle = a_1 \text{Det1} + a_2 \text{Det2} + \dots$$

If “very many” “very different” determinants are involved, correlations are “strong”

**Notice: 2 related but conceptually different issues**

- **Ground state**
- **Excitation**

**some methods optimized for ground states,  
others aimed at excitations**

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# Taxonomy of correlation: I

**Approximately free electrons:**

— **Coulomb interaction (long range)**

$$\mathbf{H}[\mathbf{Ry}] = -\frac{1}{r_s^2} \sum_i \nabla_{u_i}^2 + \frac{1}{r_s} \sum_{i \neq j} \frac{1}{|\vec{u}_i - \vec{u}_j|}$$

$r_s \sim$  **inter-electron spacing in units of bohr radius.**

**Small  $r_s$  (high density)  $\Leftrightarrow$  weak correlations  
because **Coulomb interaction is well screened****

**Graphene (and cousins): important special case**

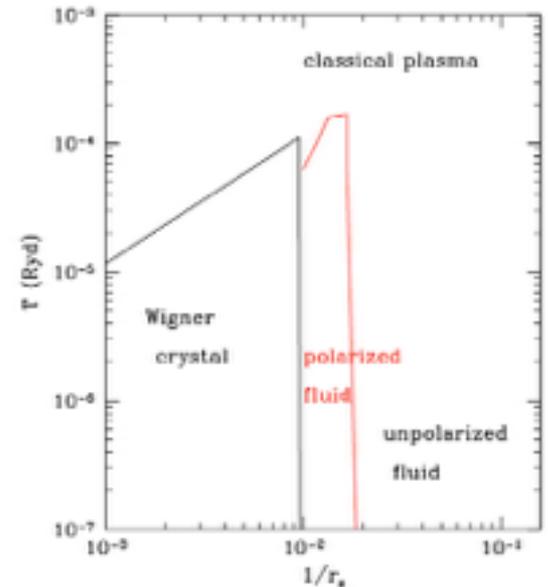
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# Coulomb physics

- Perturbation theory (RPA):  $r_s \sim 1$
- Typical wide-band metals:  $r_s \sim 2-6$
- Wigner crystal  $r_s \sim 30-80$  (dimension)

3d electron gas  
(Ceperly)



**Hartree term fixes charge distribution.  
Exchange terms control fluctuations about this.**

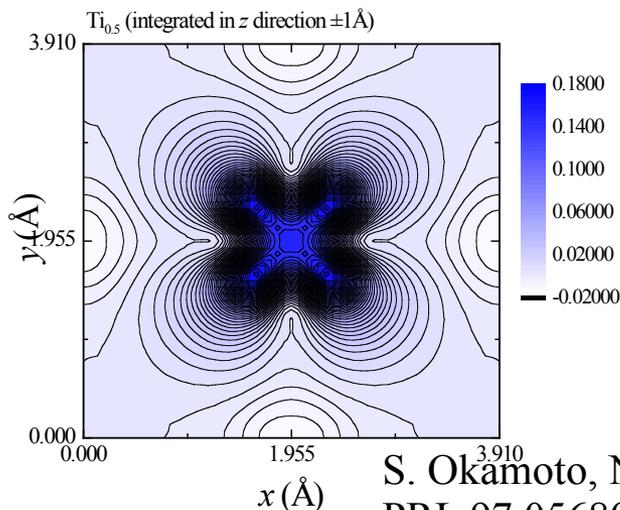
# Taxonomy of correlation: II

## Partially filled, relatively localized (tight-binding-like) orbitals

\*transition metals and their oxides (and sulfides and calcogenides): transition metal d shell

\*rare earth and actinide materials (f shell)

\*organics (effective orbital)



**\*Key role of intra-orbital interactions**

**\*Certain atomic configurations suppressed**

S. Okamoto, N, Spaldin and AJM  
PRL 97 056802 (2006)

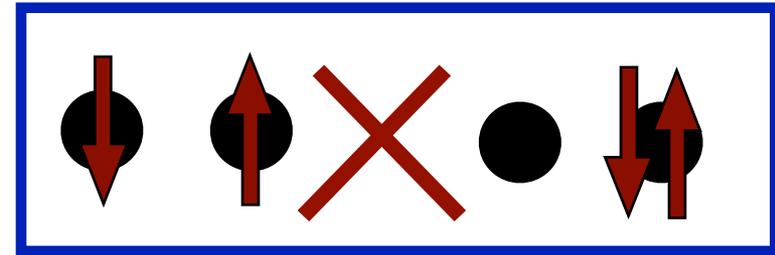
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# Taxonomy of correlation: IIa

## Mott-Hubbard.

- `Coulomb blockade' (some charge configurations suppressed)
- importance of `new' degree of freedom (here, spin)
- near commensurability of electron and lattice densities=>`jamming''



## Model `Hubbard' Hamiltonian:

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

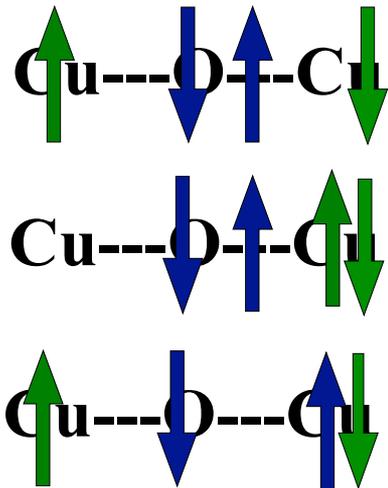
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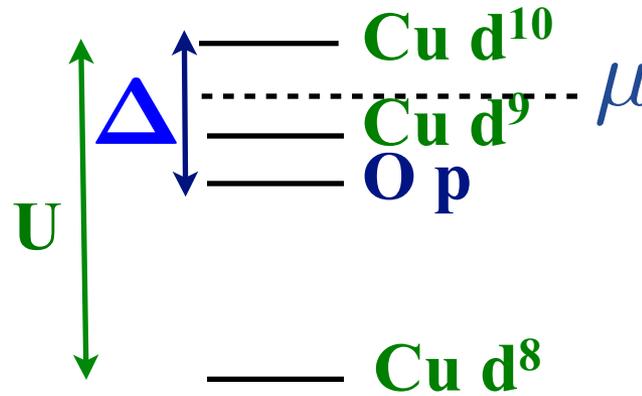
# Charge Transfer Insulators

$2d^n \Rightarrow d^{n-1}d^{n+1}$  not the only process. Ligands also important.

Fragment of  $\text{CuO}_2$   
plane



Energies



$$\Delta > U$$

Charge transfer  
insulator

**Cuprates:**

$$2d^9 \Rightarrow d^8 d^{10} \quad 8\text{eV}$$

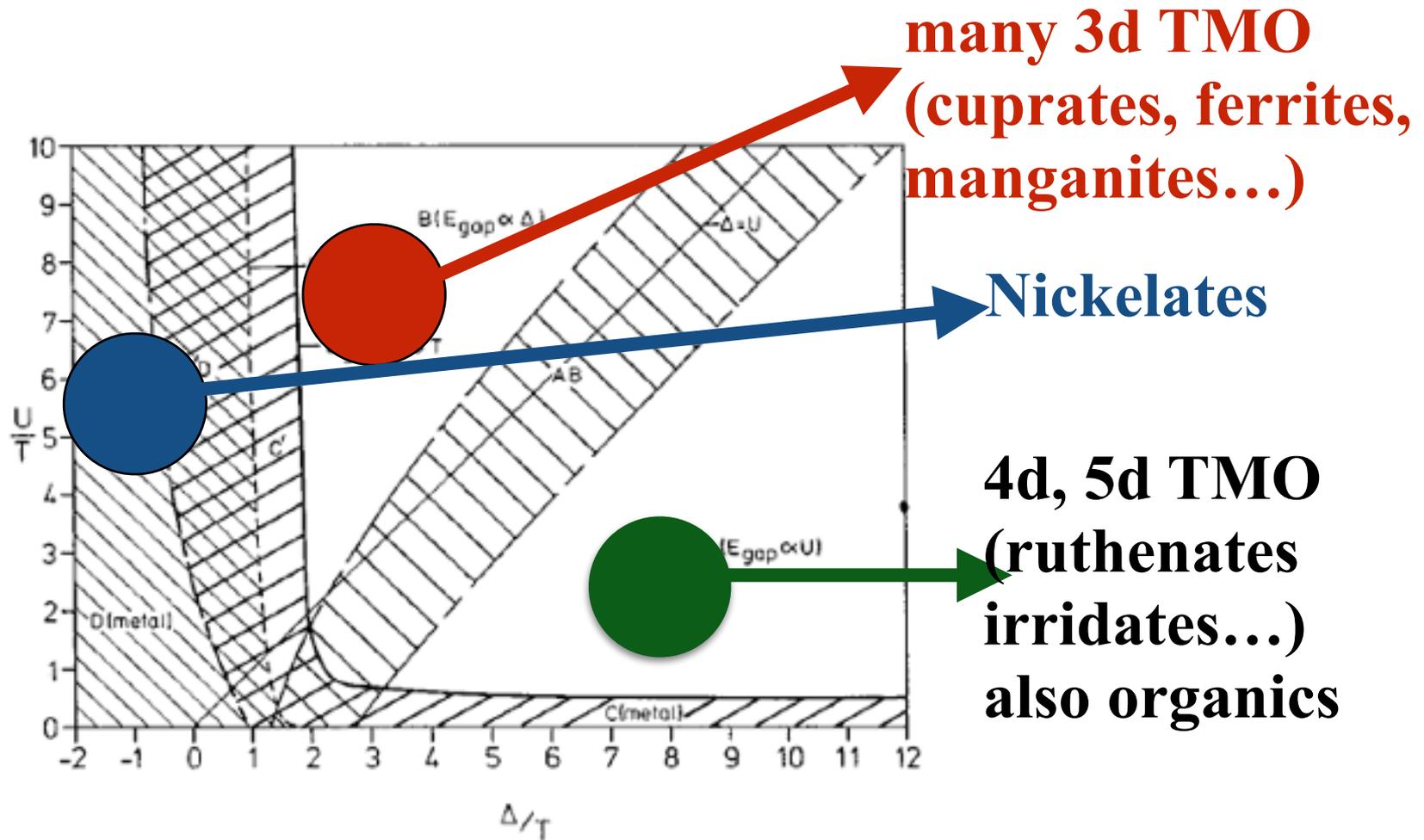
$$2d^9 \Rightarrow d^9 O p^5 d^{10} \quad 2\text{eV}$$

Zaanen, Sawatzky, Allen,  
Phys. Rev. Lett. 55, 418 (1985)

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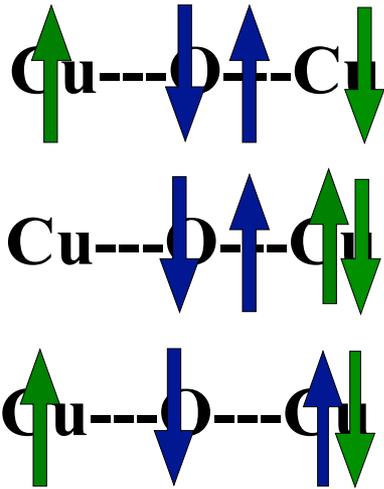
# ZSA Phase Diagram



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# Open questions:



- how much of the correlation physics of the ligand ions do we need to know
- does an effective low energy model suffice?

**Open question: in this physics, ligand to transition metal charge fluctuations are important. Do we need to include dynamics of intersite Coulomb physics**

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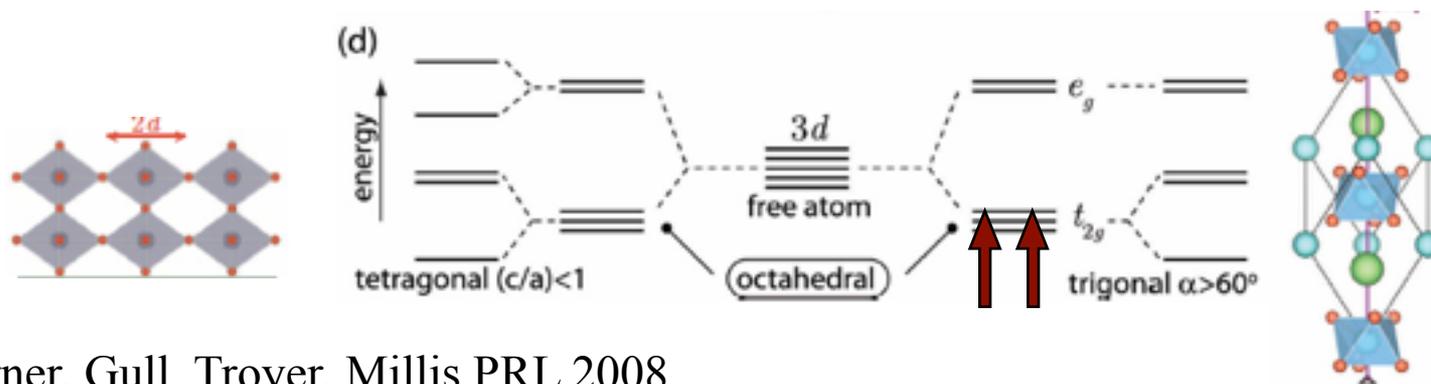
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# Taxonomy of correlation: IIb

## ‘Hunds Physics’.

- free space: 10-fold degenerate d-level.
- M electrons=> $10!/((10-M)!M!)$  states
- Ligand field and intra-orbital Coulomb interaction => some states disfavored.
- Hund’s rule: High spin states preferred=>new physics

Rondinelli and Spaldin. Adv. Mater. 23



Werner, Gull, Troyer, Millis PRL 2008

Haule and Kotliar NJP 2009

Georges, deMedici and Mravlje, Ann Rev CMP 2012

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# Correlated subspace: transition metal d orbitals

$$H_{\text{one-electron}} = \sum_a E_a c_a^\dagger c_a$$

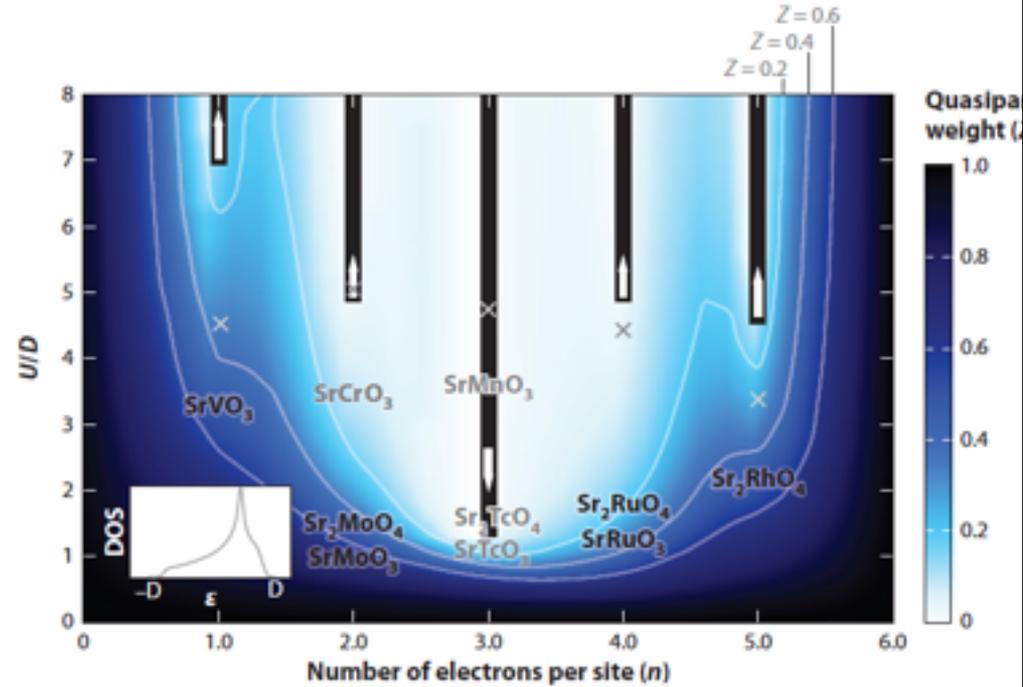
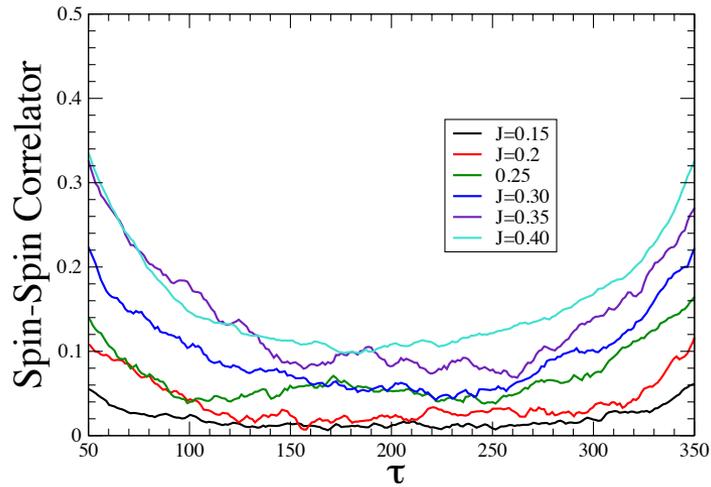
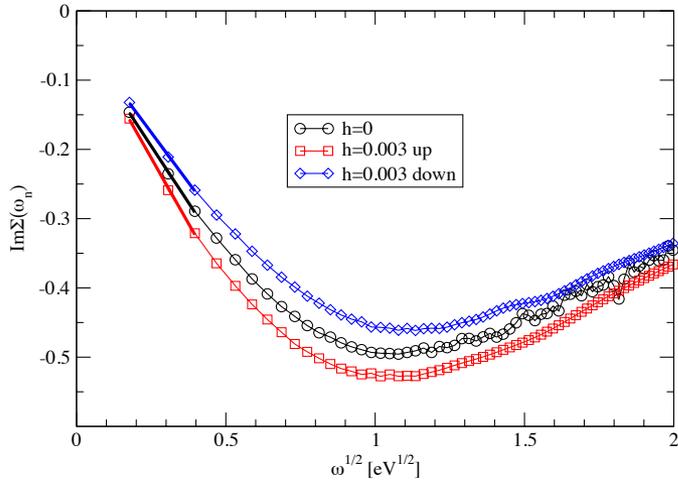
**Interaction:** Full multiplet structure of d-shell  
(here written for O(3) symmetry  $t_{2g}$  or  $e_g$ )

$$H = U \sum_a n_{a\uparrow} n_{a\downarrow} + (U - 2J) \sum_{a>b, \sigma=\uparrow, \downarrow} n_{a\sigma} n_{b\sigma} \\ + (U - 3J) \sum_{a \neq b\sigma} n_{a\sigma} n_{b\bar{\sigma}} - J \sum_{a \neq b} c_{a\uparrow}^\dagger c_{a\downarrow}^\dagger c_{b\uparrow} c_{b\downarrow} + c_{a\uparrow}^\dagger c_{b\downarrow}^\dagger c_{b\uparrow} c_{a\downarrow}$$

**U:** screened in solid—  
**J:** close to atomic limit value



# Spin Freezing



Georges, deMedici and Mravlje, Ann Rev CMP 2012

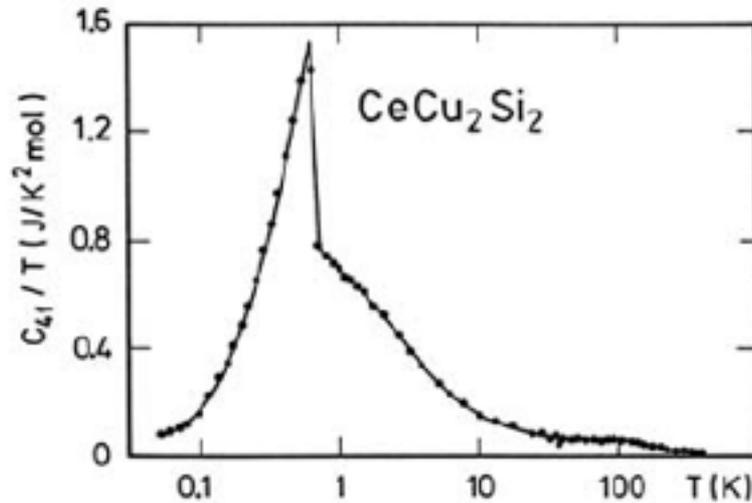
H. Dang and AJM, unpub 2014

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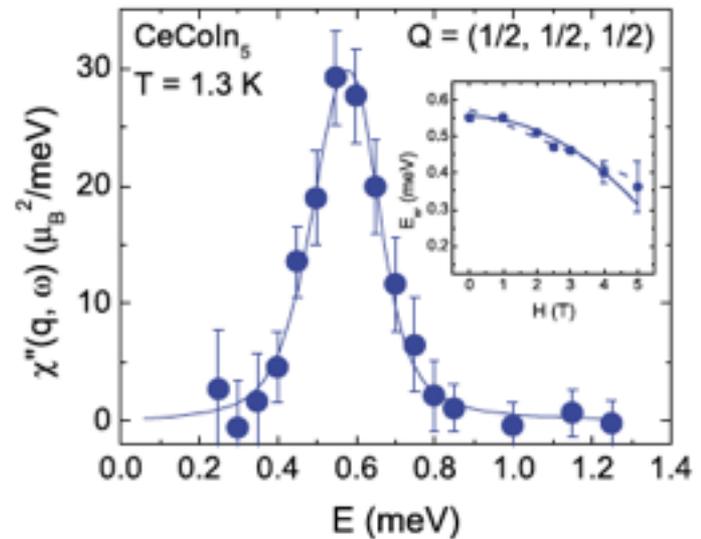
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# Taxonomy of correlation: III

## Heavy Fermions



Steglich 2012



Thompson and Fisk, 2012

**key physics—weakly correlated band coupled to slowly fluctuating local degree of freedom**

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# Taxonomy of correlation: IV

## Special cases

- one dimensional systems
- quantized hall states
- impurity models: quantum dots and molecular conductors**

....

# Impurity model: finite set of correlated orbitals coupled to bath

$$H_{\text{QI}} = \sum_{ab} d_a^\dagger E_{\text{QI}}^{ab} d_b + \text{Interactions} \quad \text{Impurity Hamiltonian}$$

$$+ \sum_{p,ab} (V_{ab}^p d_a^\dagger c_{pb} + \text{H.c.}) + H_{\text{bath}}[\{c_{pa}^\dagger c_{pa}\}] \quad \text{Coupling to bath}$$

Important part of bath: ‘hybridization function’

$$\Delta^{ab}(z) = \sum_p V_{ac}^p \left( \frac{1}{z - \epsilon_p^{\text{bath}}} \right) V_{cb}^{p,\dagger}$$

# Solving impurity models

Typically need  $G$  at ‘all’ interesting frequencies computed with uniform accuracy over whole relevant frequency range.

This is challenging.

Challenge is much more severe if

$$\left[ \hat{\Delta}, \hat{E} \right] \neq 0$$

i.e. if electron can go off impurity and come back to a different state

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# What's the problem?

P.A.M. Dirac, Proc. Roy. Soc. 1929



“The fundamental laws necessary for the mathematical treatment of a large part of physics and the whole of chemistry are known...”

o o o

“The difficulty lies **only** in the fact that these laws lead to equations too complex to be solved.”

“It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed.”

# Computational cost

- **M atoms per unit cell**
- **Energy cutoff=>L orbitals/atom**
- **Retain N unit cells**

**Hilbert Space Dimension** =  $2^{M \times L \times N}$

**Interaction terms (4 center integrals)**  $\sim (M \times L)^4 \times N^3$

**=>exponential times large power-law prefactor**

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# Fermion sign

\*electrons are fermions: wave function is **antisymmetric**

$$\psi(r_1, \sigma_1; r_2, \sigma_2; \dots) = -\psi(r_2, \sigma_2; r_1, \sigma_1; \dots)$$

**Quantum mechanics entangles electron coordinates over large distances**

**=>severe numerical complications**

# What do you do

**Hilbert Space  
Dimension**

$$= 2^{M \times L \times N}$$

**Interactions**

$$\sim (M \times L)^4 \times N^3$$

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# What do you do

**Hilbert Space  
Dimension**

$$= 2^{M \times L \times N}$$

**Interactions**

$$\sim (M \times L)^4 \times N^3$$

**Avoid the problem: density  
functional band theory  
(numerical task—essentially,  
invert a large matrix)**

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# OR

**Hilbert Space  
Dimension**

$$= 2^{M \times L \times N}$$

**Interactions**

$$\sim (M \times L)^4 \times N^3$$

- **Embedding (analyse only subset of matrix elements)**
  - DMFT (or DFT+U)
  - DMET
  - SEET
- **Model system (e.g. Hubbard model)=>**
  - minimize number of interaction parameters
- **Find correct corner of Hilbert Space**
  - CI and generalizations
  - DMRG/MPS
- **Explore Hilbert space stochastically**

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# Density functional theory

## Two aspects:

- **algorithm for ground state energy and density**
- **statement about (approximation to) ground state wave function and excitations => base for more sophisticated theory**

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# From a formal point of view

Hyowon Park, Andrew J. Millis, Chris A. Marianetti, Phys. Rev. B90, 235103 (2014).

Hyowon Park, Andrew J. Millis, and Chris A. Marianetti, Phys. Rev. B92 035146 (2015).

## DFT as functional of density and conjugate potential

$$\Phi[\{\mathbf{V}^{\mathbf{H}-\mathbf{x}\mathbf{c}}, \rho\}] = \text{Tr} \left[ \ln \left[ \partial_\tau - \frac{1}{2} \nabla^2 - \mathbf{V}^{\text{ext}}(\mathbf{r}) - \mathbf{V}^{\mathbf{H}-\mathbf{x}\mathbf{c}}(\mathbf{r}) \right]^{-1} \right] \\ + \Phi_{\text{HK}}[\{\rho\}] - \int \mathbf{d}^3\mathbf{r} \mathbf{V}^{\mathbf{H}-\mathbf{x}\mathbf{c}}(\mathbf{r}) \rho(\mathbf{r})$$

**stationarity:**

$$\frac{\delta \Phi}{\delta \mathbf{V}^{\mathbf{H}-\mathbf{x}\mathbf{c}}} = \mathbf{0} \Rightarrow \rho(\mathbf{r}) = \text{Tr} \left[ \left( \partial_\tau - \frac{1}{2} \nabla^2 - \mathbf{V}^{\text{ext}} - \mathbf{V}^{\mathbf{H}-\mathbf{x}\mathbf{c}} \right)^{-1} \right]$$

$$\frac{\delta \Phi}{\delta \rho} = \mathbf{0} \Rightarrow \mathbf{V}^{\mathbf{H}-\mathbf{x}\mathbf{c}} = \frac{\delta \Phi_{\text{HK}}}{\delta \rho}$$

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**Stationarity with respect to variations of density and  $V^{\text{H-xc}}$  yields EXACT ground state energy and electron density if EXACT exchange-correlation potential is known**

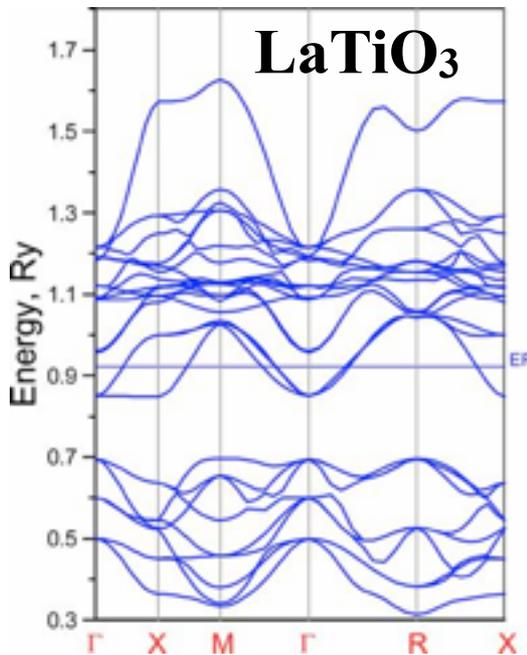
$$\frac{\delta \Phi_{\text{HK}}(\{\rho\})}{\delta \rho(\mathbf{r})} = V^{\text{H-xc}}(\{\rho\}, \mathbf{r})$$

**In practice, exact  $V$  not known;  
approximation is needed**

**Question: how good is the approximation**

# Kohn-Sham bands

$$\frac{\delta\Phi}{\delta\mathbf{V}^{\text{H-xc}}} = 0 \Rightarrow \rho(\mathbf{r}) = \text{Tr} \left[ \left( \partial_{\tau} - \frac{1}{2}\nabla^2 - \mathbf{V}^{\text{ext}} - \mathbf{V}^{\text{H-xc}} \right)^{-1} \right]$$

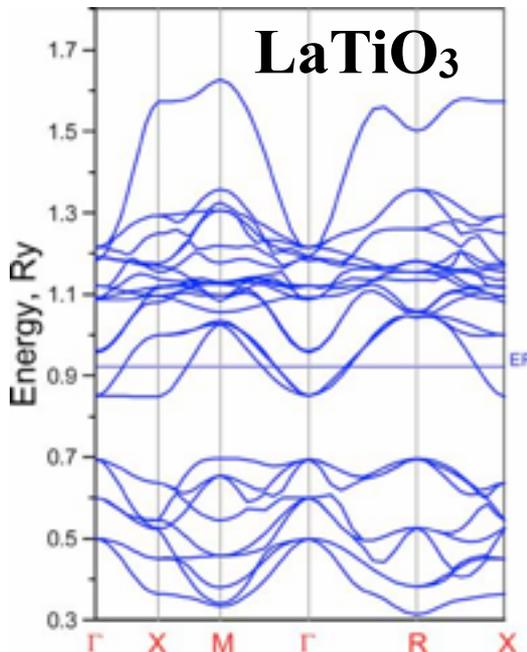


**Evaluating the trace $\Leftrightarrow$ solving a single-particle Schroedinger equation (the “Kohn-Sham equation”)**

[http://dmft.rutgers.edu/LDA/lmto/lmto\\_run.htm](http://dmft.rutgers.edu/LDA/lmto/lmto_run.htm)

# Kohn-Sham bands

$$\frac{\delta\Phi}{\delta\mathbf{V}^{\text{H-xc}}} = 0 \Rightarrow \rho(\mathbf{r}) = \text{Tr} \left[ \left( \partial_{\tau} - \frac{1}{2}\nabla^2 - \mathbf{V}^{\text{ext}} - \mathbf{V}^{\text{H-xc}} \right)^{-1} \right]$$



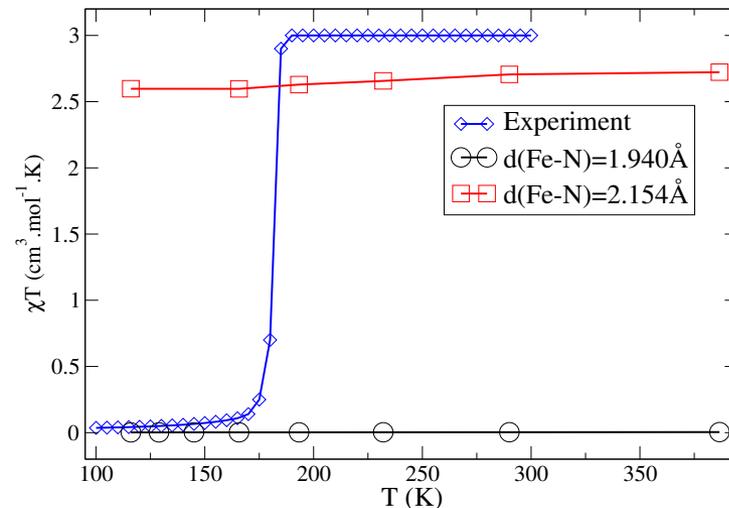
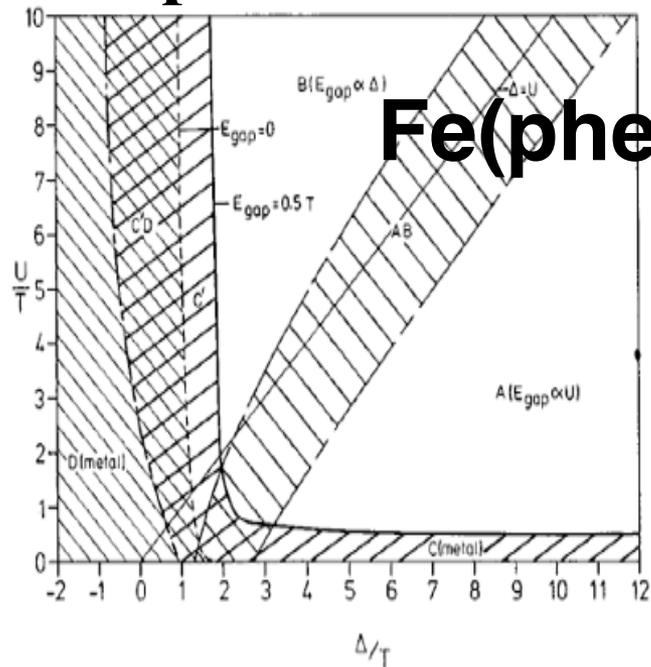
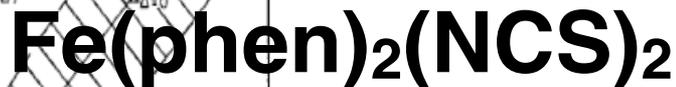
## Questions:

- is the single Slater-determinant of occupied Kohn-Sham states a good approximation to the ground state wave function
- are the eigenvalues of the Kohn-Sham Hamiltonian good approximations to transition energies

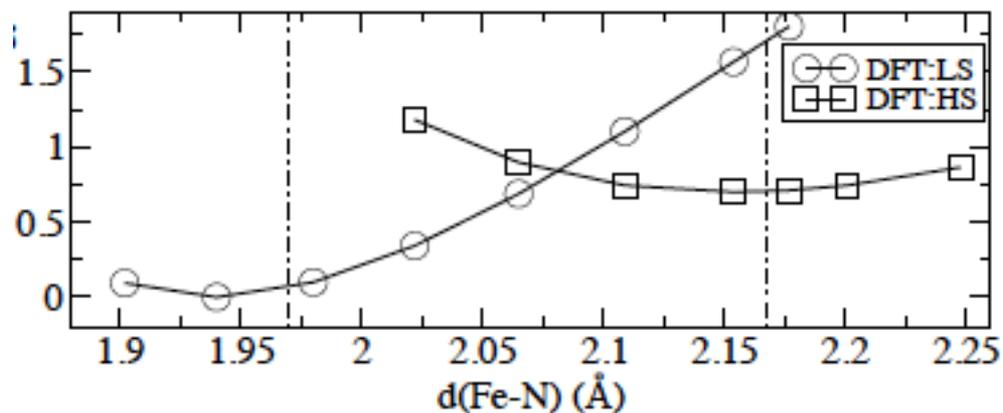
[http://dmft.rutgers.edu/LDA/lmto/lmto\\_run.htm](http://dmft.rutgers.edu/LDA/lmto/lmto_run.htm)

# Limitations of DFT

## Spin Crossover Molecule



## DFT: overestimates energy diff



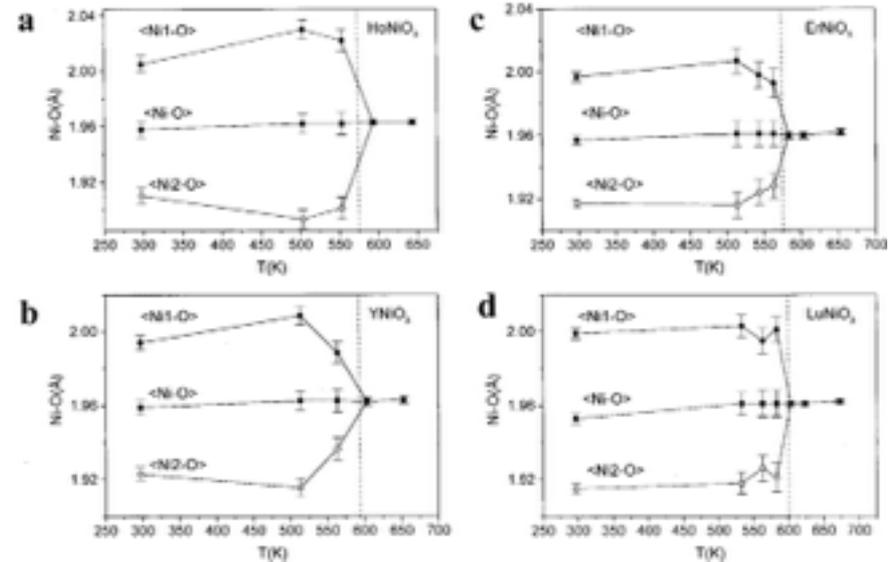
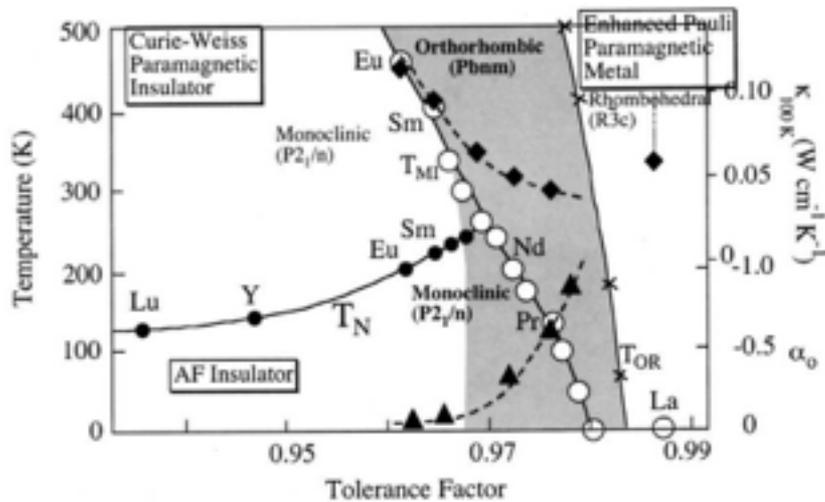
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# Limitations of DFT

## Rare earth nickelates: $\text{RNiO}_3$

For all R except La: materials are insulating and bond-disproportionated

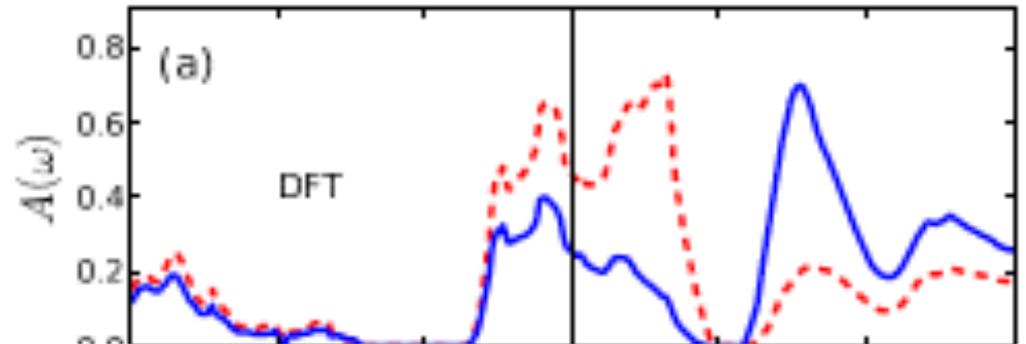
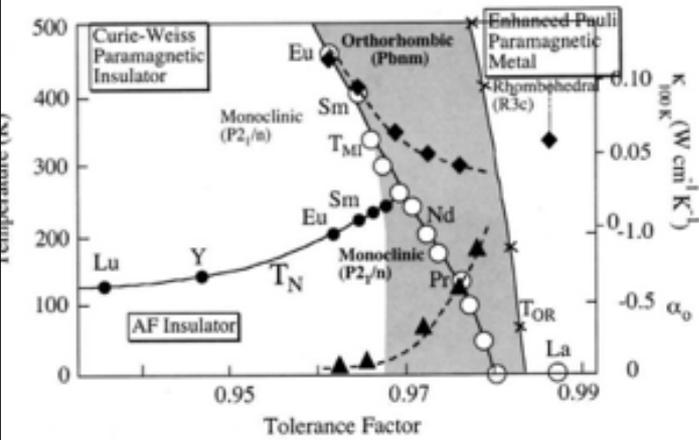


**DFT: does not predict structural distortion for any R**  
**predicts metallic behavior for all R**

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# In experimental structure DFT predicts metal

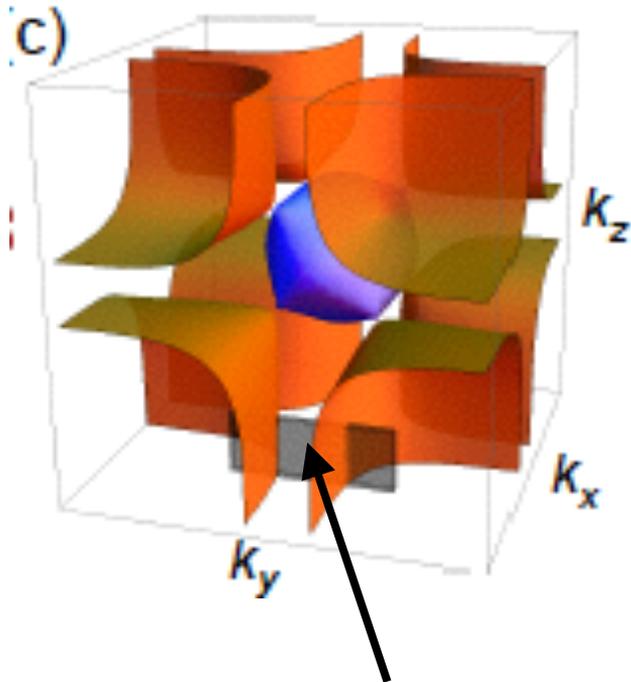


H. Park, AJM, and C. Marianetti,  
Phys. Rev. Lett. 109, 156402 (2012)

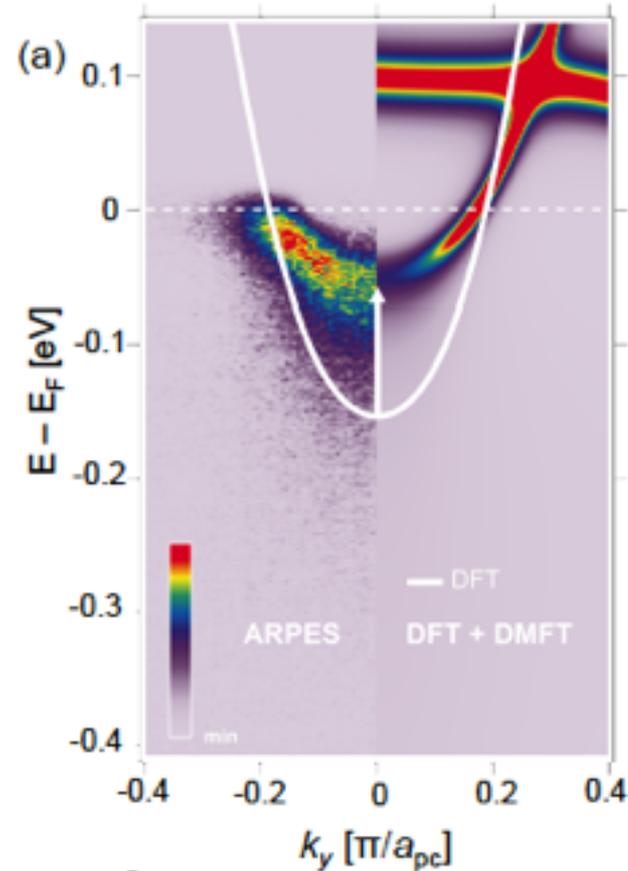
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# Metallic $\text{LaNiO}_3$ : DFT makes quantitative errors in bands



**Momentum cut**



E. A. Nowadnick, J. P. Ruf, H. Park, P. D. C. King,  
D. G. Schlom, K. M. Shen, A. J. Millis, Phys. Rev.  
B92, 245109 (2015).

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**=> Need beyond DFT method**

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# OR

**Hilbert Space  
Dimension**

$$= 2^{M \times L \times N}$$

**Interactions**

$$\sim (M \times L)^4 \times N^3$$

- **Embedding (analyse only subset of matrix elements)**
  - DMFT (or DFT+U)
  - DMET
  - SEET
- **Model system (e.g. Hubbard model) =>**
  - minimize number of interaction parameters
- **Find correct corner of Hilbert Space**
  - CI and generalizations
  - DMRG/MPS
- **Explore Hilbert space stochastically**

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# +DMFT

**See also DMET (self-consistently embedded density matrix)**

- G. Knizia, G. K.-L. Chan; Phys. Rev. Lett., 109, 186404 (2012)
- G. Knizia, G.K.-L. Chan; J. Chem. Theory Comput., 9, 1428 (2013)

**and SEET (self-energy embedding theory—conceptually DFT +DMFT but (a) NOT built on DFT and (b) not necessarily built on local orbitals**

- TN Lan, AA Kananenka, D Zgid, The Journal of chemical physics 143 (24), 241102 and arXiv:1606.07454

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# **DFT+DMFT now ~20 years old**

**Proposal: Lichtenstein/Katsnelson late 1990s**

**Key papers:**

- **Georges 2004 Windsor notes**
- **Kotliar et al RMP 2006**
- **Held and Vollhardt 2006**

# DFT+DMFT: quad variable functional theory- DFT plus many-body theory of correlated subspace

$$\Phi[\{\mathbf{V}^{\text{H-xc}}, \rho; \Sigma_{\text{corr}}, \mathbf{G}_{\text{corr}}\}] =$$

$$\text{Tr} \left[ \ln \left[ \partial_\tau - \frac{1}{2} \nabla^2 - \mathbf{V}^{\text{ext}}(\mathbf{r}) - \mathbf{V}^{\text{H-xc}}(\mathbf{r}) - \mathbf{P}_{\text{corr}} \Sigma_{\text{corr}} \mathbf{P}_{\text{corr}} \right]^{-1} \right]$$

$$+ \Phi_{\text{DFT+DMFT}}[\{\mathbf{G}_{\text{corr}}, \rho\}] - \text{Tr}[\Sigma_{\text{corr}} \mathbf{G}_{\text{corr}}] - \int d^3\mathbf{r} \mathbf{V}^{\text{H-xc}}(\mathbf{r}) \rho(\mathbf{r})$$

## Stationarity:

$$\frac{\delta \Phi_{\text{DFT+DMFT}}}{\delta \rho(\mathbf{r})} = \mathbf{V}^{\text{H-xc}}(\mathbf{r})$$

$$\frac{\delta \text{Tr}[\ln]}{\delta \mathbf{V}^{\text{H-xc}}(\mathbf{r})} \equiv \mathbf{G}(\mathbf{r}, \mathbf{r}; \tau \rightarrow 0^-) = \rho(\mathbf{r})$$

$$\frac{\delta \Phi_{\text{DFT+DMFT}}}{\delta \mathbf{G}_{\text{corr}}} = \Sigma_{\text{corr}}$$

$$\frac{\delta \text{Tr}[\ln]}{\delta \Sigma_{\text{corr}}} \equiv \mathbf{P}_{\text{corr}} \mathbf{G} \mathbf{P}_{\text{corr}} = \mathbf{G}_{\text{corr}}$$

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**formally exact**

**Approximations needed in two places**

$$\frac{\delta\Phi_{\text{DFT+DMFT}}}{\delta\rho(\mathbf{r})} = V^{\text{H-xc}}(\mathbf{r}) \quad (\text{getting } V^{\text{H-xc}} \text{ from charge})$$

$$\frac{\delta\Phi_{\text{DFT+DMFT}}}{\delta\mathbf{G}_{\text{corr}}} = \Sigma_{\text{corr}} \quad (\text{formulating and solving many body problem})$$

**Note: formulating the correlation problem includes defining orbitals and specifying interactions**

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# Self Energy

$$\mathbf{P}_{\text{corr}} \boldsymbol{\Sigma}_{\text{corr}} \mathbf{P}_{\text{corr}}$$

is a matrix acting on a pre-identified subspace of correlated orbitals

$V^{\text{H-xc}}(\mathbf{r})$  also has matrix elements in correlated space

$\Rightarrow$  "double counting"

$$\frac{\delta \Phi_{\text{DFT+DMFT}}}{\delta \mathbf{G}_{\text{corr}}} = \boldsymbol{\Sigma}_{\text{corr}}$$

$$\frac{\delta \text{Tr}[\ln]}{\delta \boldsymbol{\Sigma}_{\text{corr}}} \equiv \mathbf{P}_{\text{corr}} \mathbf{G} \mathbf{P}_{\text{corr}} = \mathbf{G}_{\text{corr}}$$

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# What is done in practice

$$\Phi_{\text{DFT+DMFT}}[\rho, \mathbf{G}_{\text{corr}}] = \Phi_{\text{HK}}[\rho] + \Phi_{\text{DMFT}}[\mathbf{G}_{\text{corr}}] - \Phi_{\text{DC}}[\mathbf{G}_{\text{corr}}]$$

- $V^{\text{H-xc}}$  from DFT using density from full many body solution
- Correlated subspace: defined via Wannier or projector
- $\mathbf{G}_{\text{corr}}$  from DMFT procedure (single-site+'Slater-Kanamori' U/J interactions (c-RPA))
- **Double counting term**

**Note: DFT+U is DFT+DMFT with impurity model solved in Hartree approximation**

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# What is done in practice

$$\Phi_{\text{DFT+DMFT}}[\rho, \mathbf{G}_{\text{corr}}] = \Phi_{\text{HK}}[\rho] + \Phi_{\text{DMFT}}[\mathbf{G}_{\text{corr}}] - \Phi_{\text{DC}}[\mathbf{G}_{\text{corr}}]$$

- $V^{\text{H-xc}}$  from DFT using density from full many body solution
- Correlated subspace: defined via Wannier or projector
- $\mathbf{G}_{\text{corr}}$  from **single-site** DFMT procedure (single-site+'Slater-Kanamori' U/J interactions (c-RPA))
- **Double counting term**

=>energy as function of atomic position now available  
=>forces and relaxation (Leonov, Haule, Park)

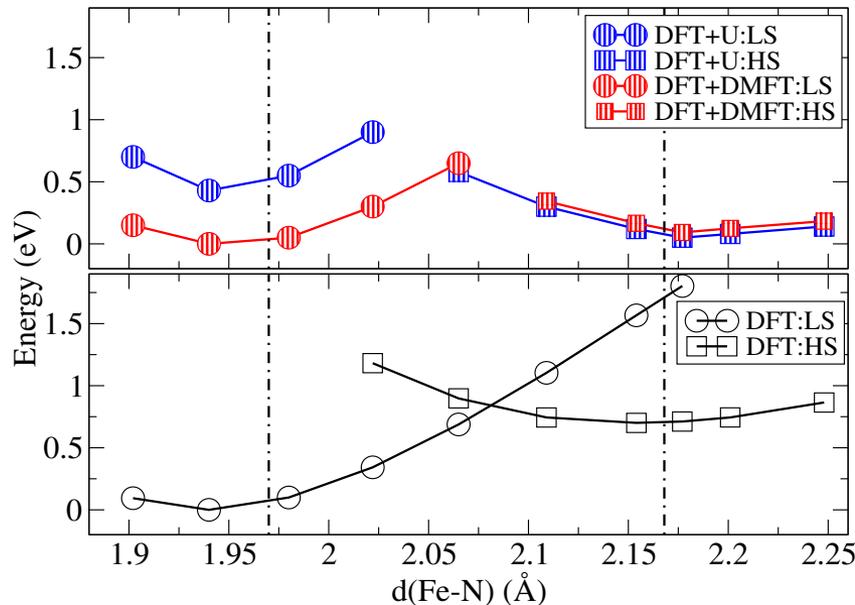
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# Beyond DFT: the spin crossover molecule

Jia Chen, AJM and C. Marianetti, Phys. Rev. B91 241111 (2015)

**DFT+U: gets energy of high spin state right but gets energy of low spin state wrong (for reasonable  $U \sim 5\text{eV}$ )**



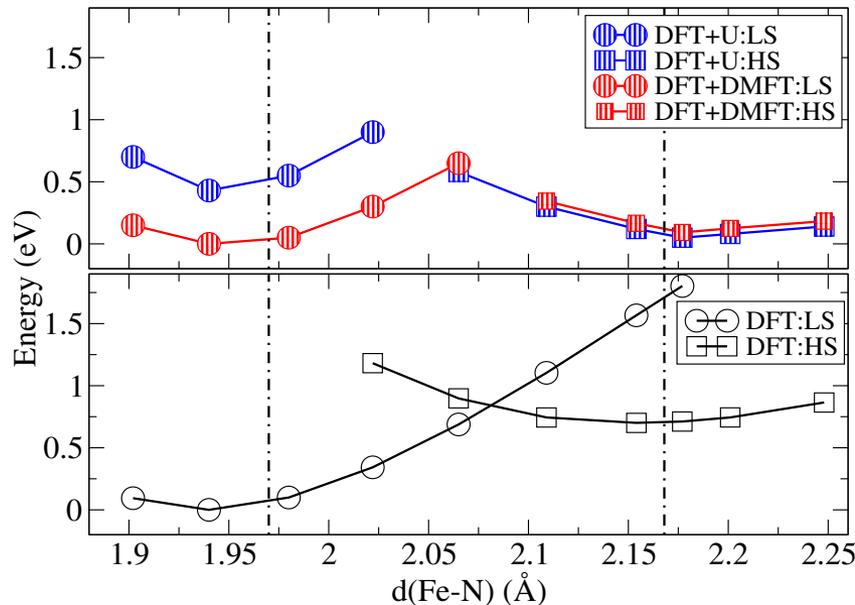
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# Application to Spin Crossover Molecules

Jia Chen, AJM and C. Marianetti, Phys. Rev. B91 241111 (2015)

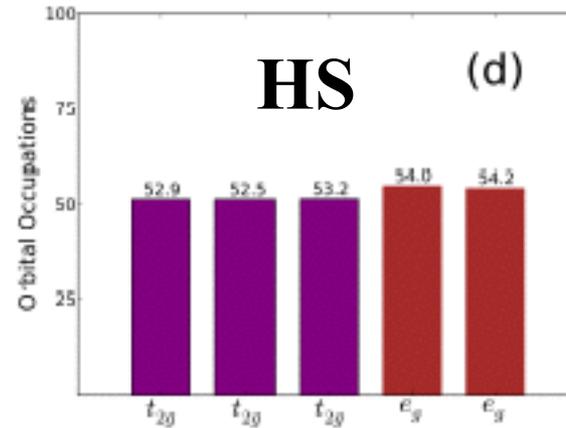
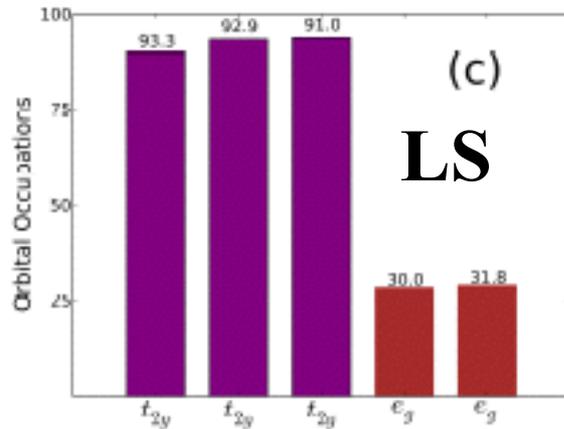
## DFT+DMFT “works”!



**DFT+U: gets energy of high spin state right but gets energy of low spin state wrong**

**DMFT: fixes problem with energy of low spin state.**

# Occupation Histograms



**Low Spin:  $N_d=6.7$**   
 **$t_{2g}$  fully occupied.**  
**Correlation physics affects**  
**charge flucfs into  $e_g$**   
**=> ``multireference''**

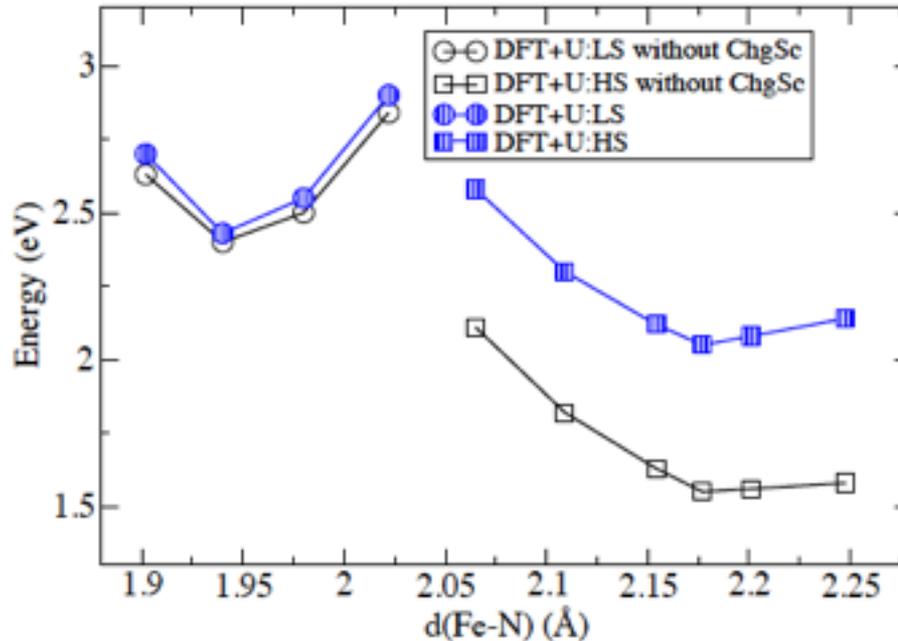
**High Spin:  $N_d=5.3$**   
**Majority spin orbitals occupied**  
**Minority spin orbitals empty.**  
**=> ``single reference''.**  
**DFT+U is OK**

**DMFT: captures energetics of valence**  
**fluctuation in correlated environment**

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# Role of charge self-consistency

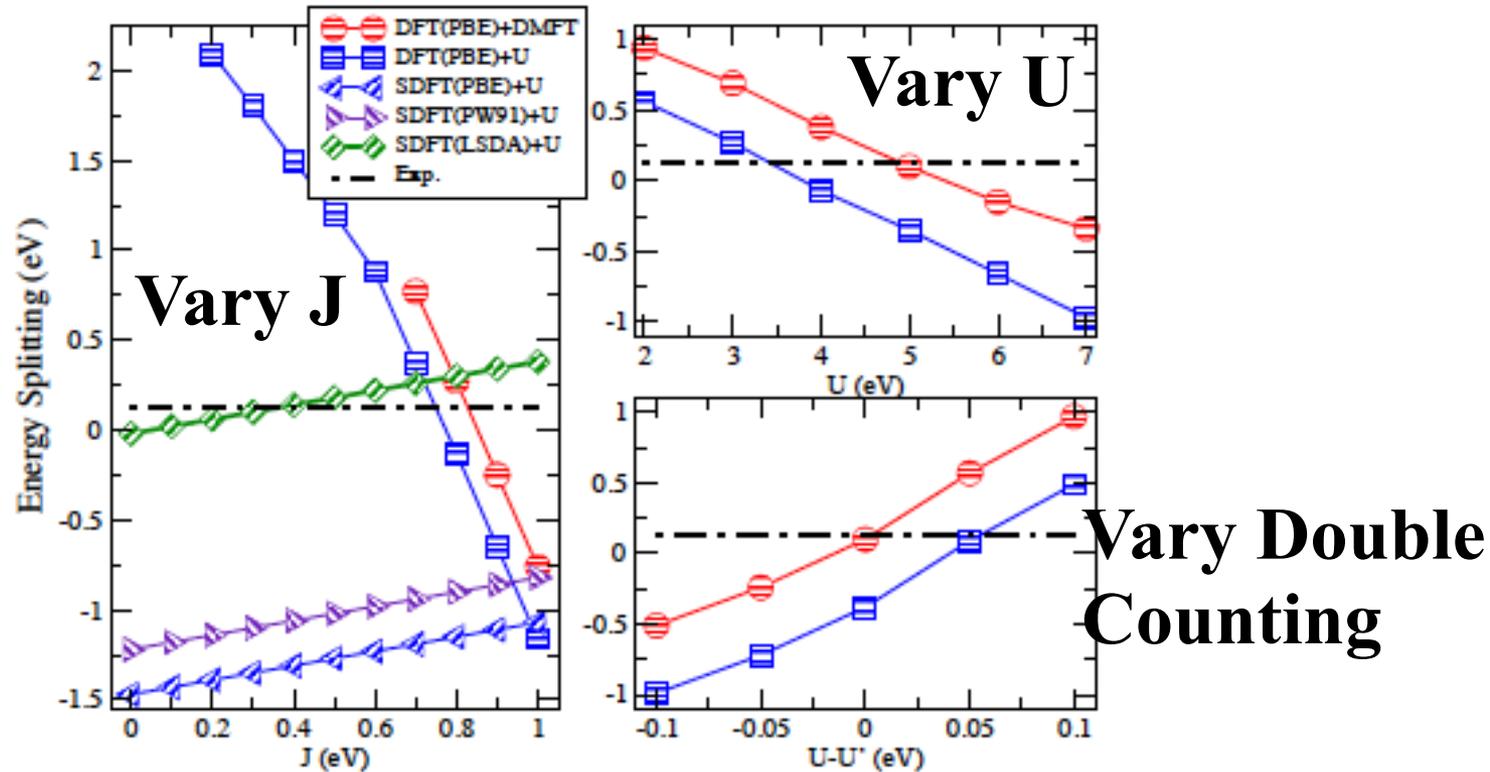


**$N_d$  in starting DFT is  $\sim 6.8$ . d-occupancy in HS state is  $N_d \sim 5.3$ , much less than DFT value. Full charge self consistency allows charge on ligand to relax to screen E-field from change in d occupancy; does not change  $N_d$  much**

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# Sensitivity to interaction strength

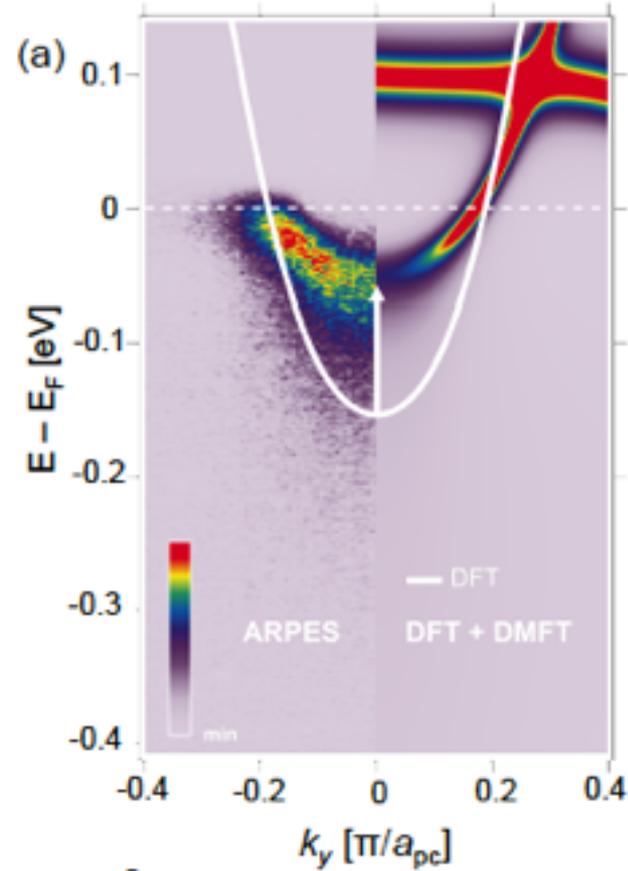
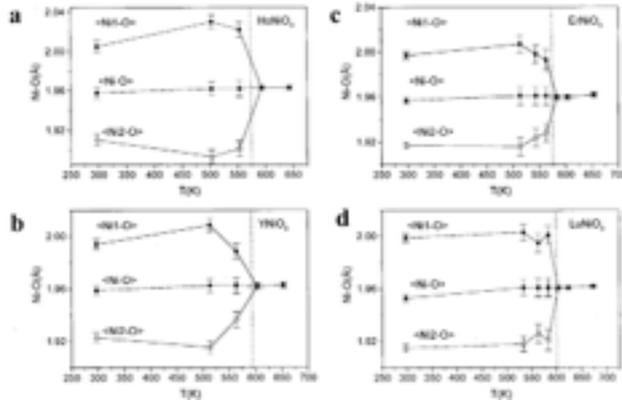
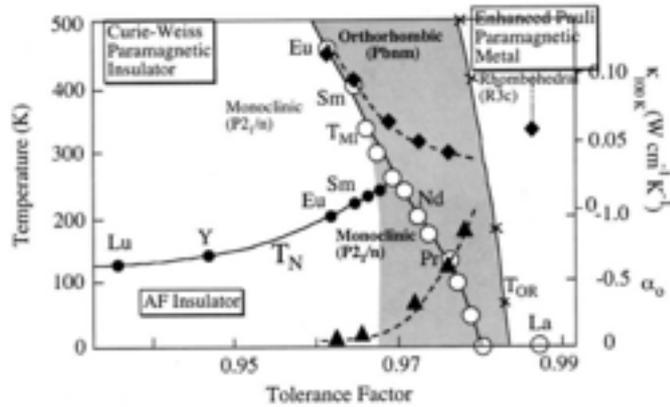


**DMFT: correct energy difference for reasonable  $U, J$**   
**Right choice of double counting crucial**  
**Method not yet at chemical accuracy**

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# DFT+DMFT for rare earth nickelates



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# DFT+DMFT: technicalities

DFT: VASP GGA; PAW, 6x6x6 (exc 8x8x8 for LaNiO<sub>3</sub>) k-point mesh; 600 eV energy cutoff

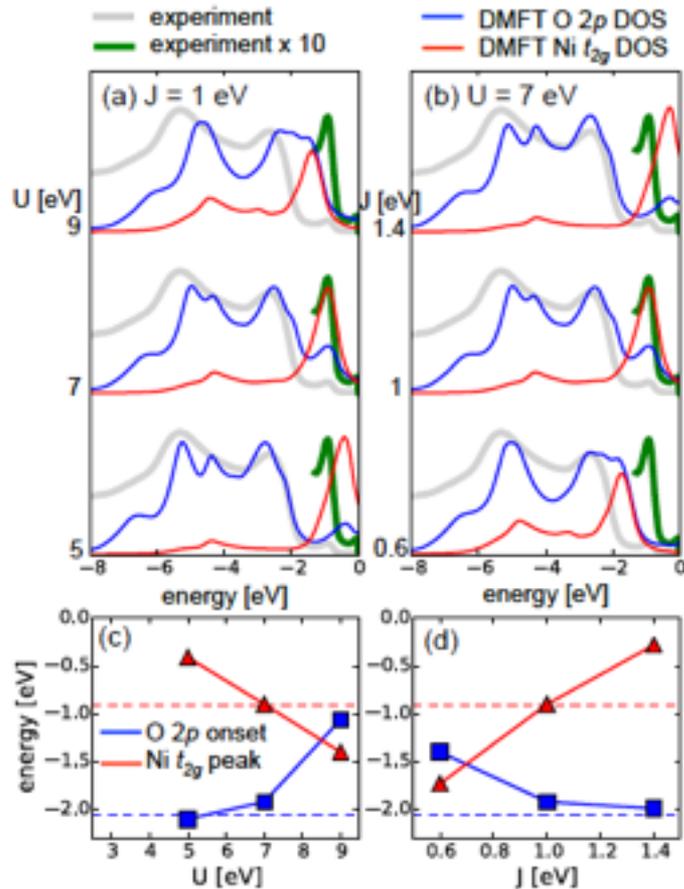
DMFT: Atomic d-orbital (MLFW from d-p complex) Slater-Kanamori interaction,  $U=5\text{eV}$ ,  $U'=4.8\text{eV}$   $J=0.67\text{eV}$ , single-site, CT-QMC

Compute energy along 1d path interpolating from experimental high-T to experimental low-T structure

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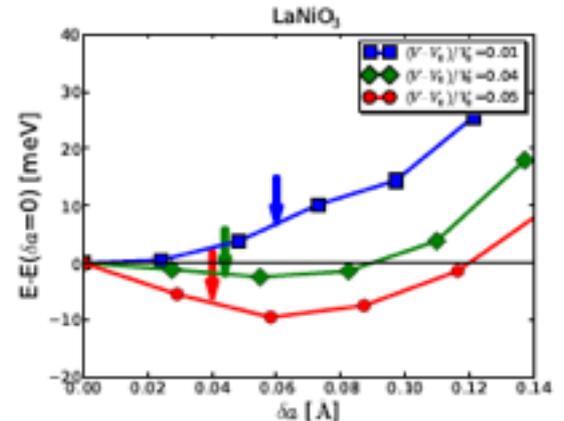
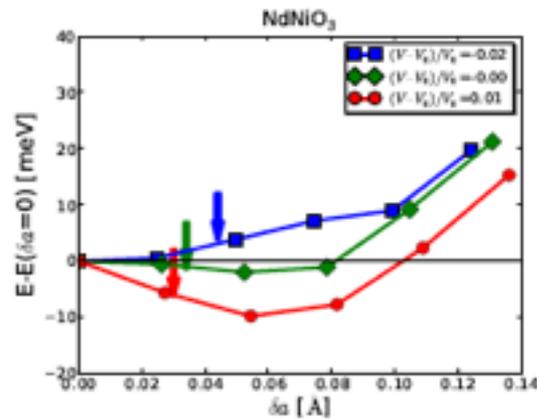
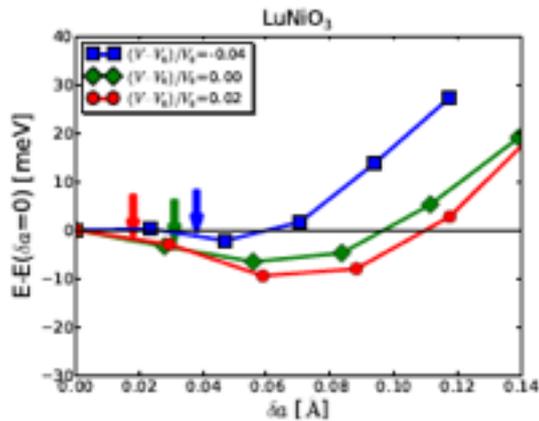
# Onsite interaction and double counting determined phenomenologically



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# Energy vs lattice distortion at different unit cell volumes

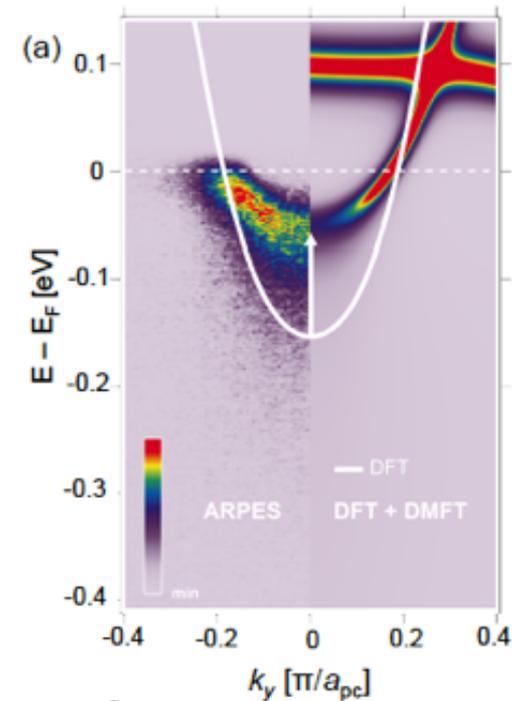
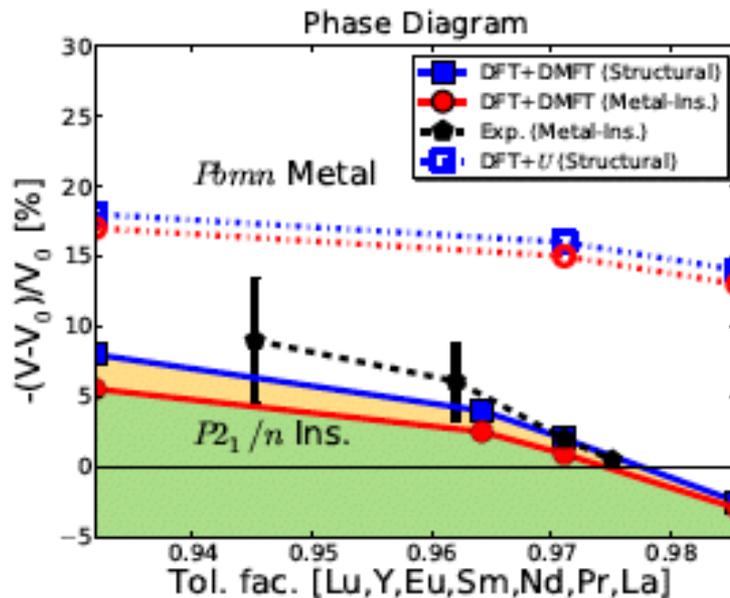


(Note colors mean different things on different plots)

# Method gets correct ground state structural/ metal-insulator phase diagram

Hyowon Park, Andrew J. Millis, Chris A. Marianetti, Phys. Rev. B90, 235103 (2014).

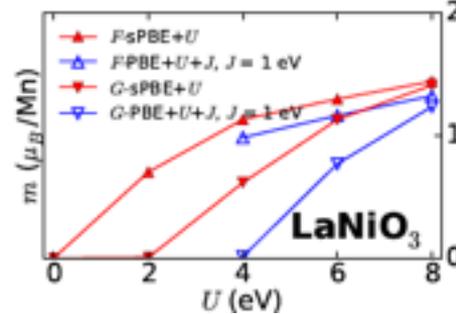
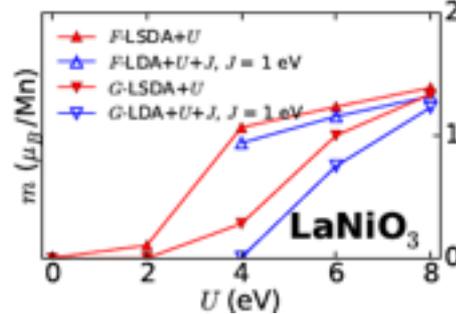
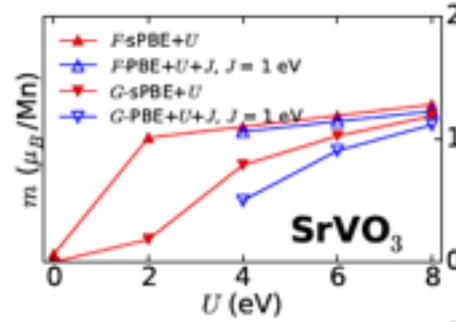
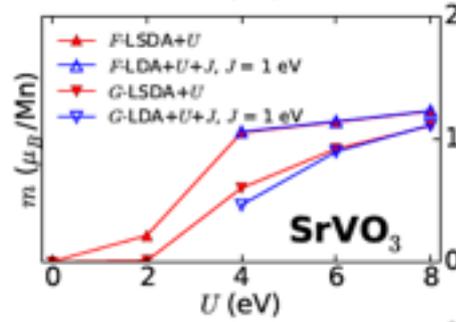
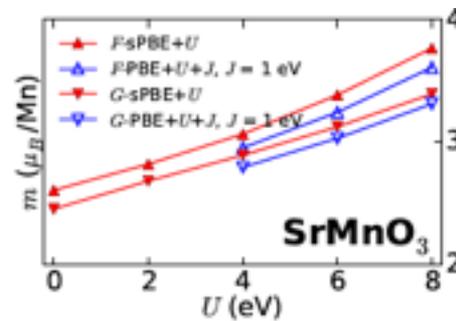
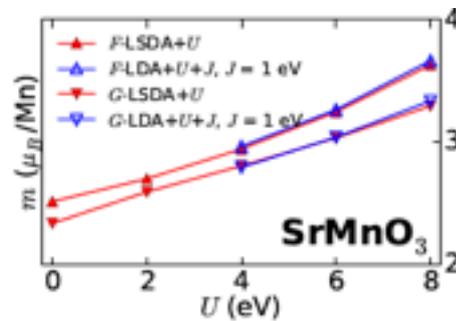
E. A. Nowadnick, J. P. Ruf, H. Park, P. D. C. King, D. G. Schlom, K. M. Shen, A. J. Millis, Phys. Rev. B92, 245109 (2015).



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# Does the DFT Functional you use make a difference?



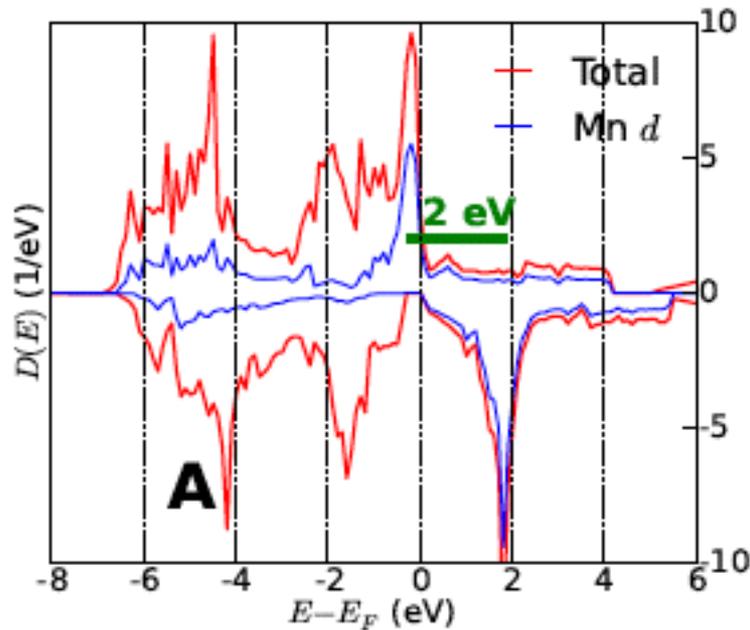
**DFT+U: small diff**

**spin-polarised DFT  
+U: much larger  
differences**

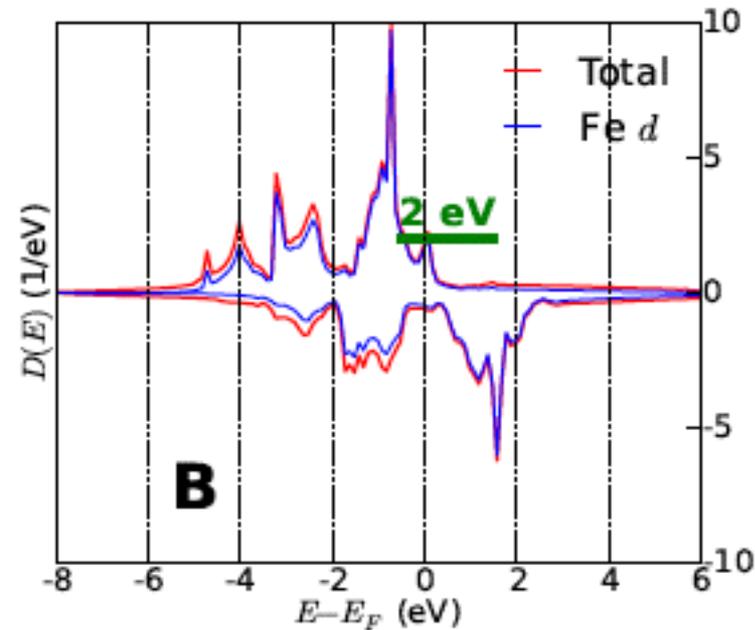
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# spin-dependent functionals have a large intrinsic Hunds coupling



**SrMnO<sub>3</sub>**



**Fe**

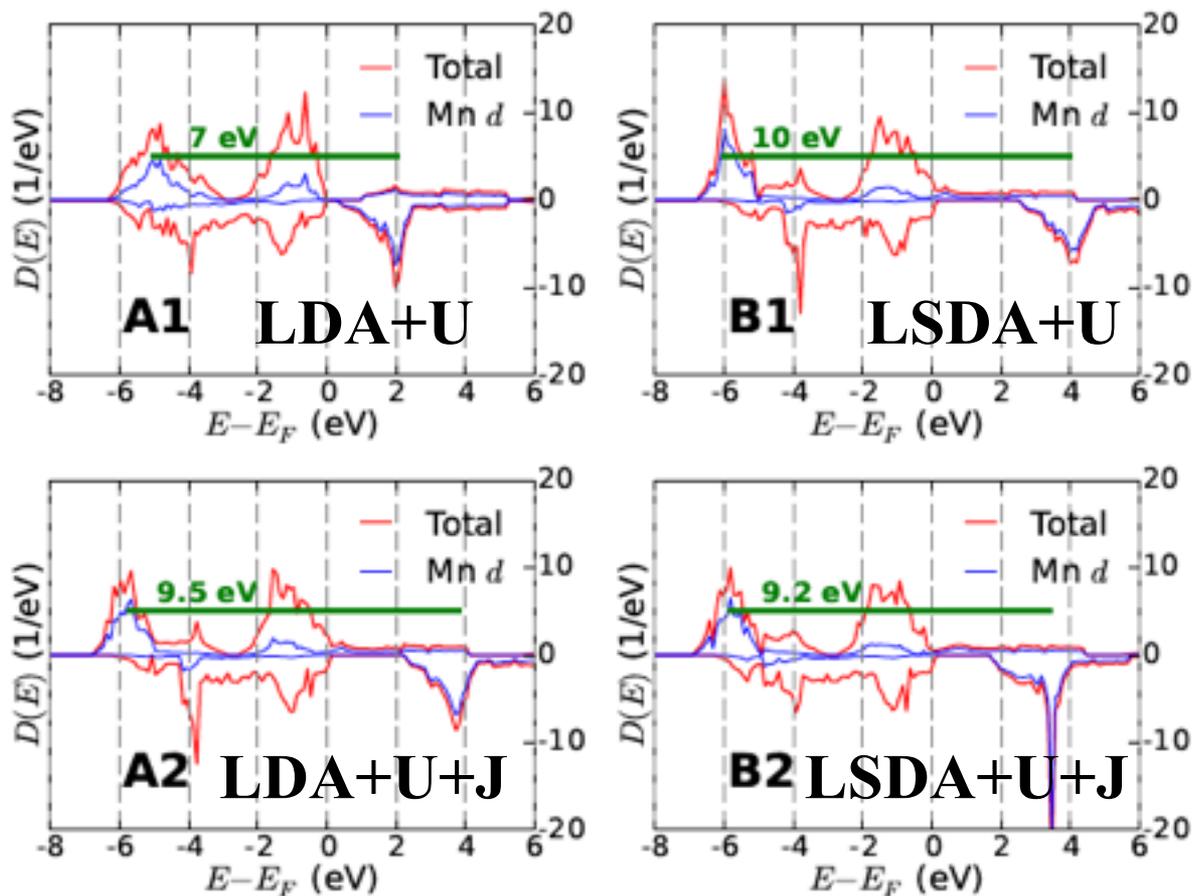
H, Chen and AJM, Phys. Rev. B93, 045133 (2016)

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# Intrinsic “J” interacts badly with +U/+J methods



**SrMnO<sub>3</sub>**

**U=6eV, J=1eV**

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# In practice: double counting is a hartree term in self energy

$$\Sigma_{\text{corr}} \rightarrow \Sigma_{\text{DMFT}}(\omega) - V_{\text{DC}}$$

fixes mean d-level energy relative to other levels; in particular, to  $O_{2p}$

Standard approach: 'Fully Localized Limit' form

$$V_{\text{DC}} = U' \langle N_d \rangle - \frac{5}{2} J \langle N_d \rangle$$

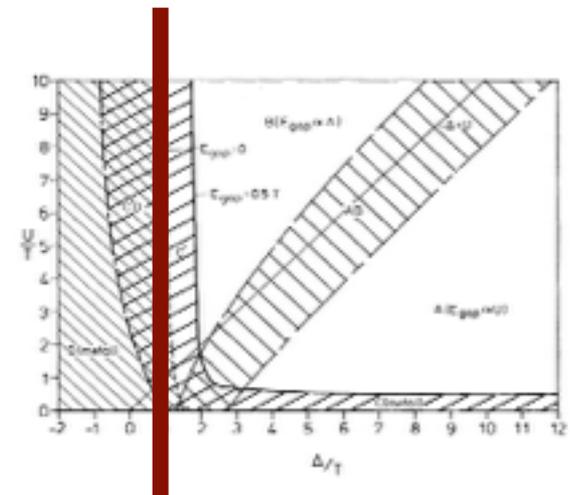
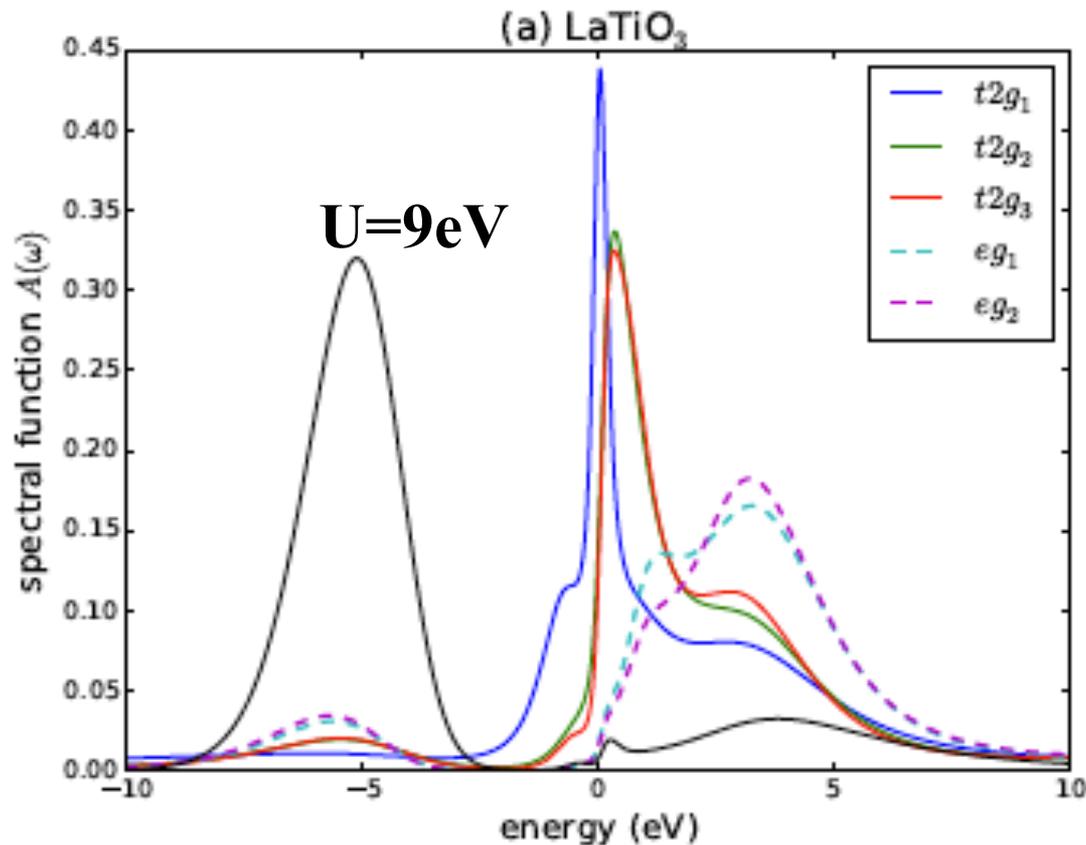
Traditional choice:  $U'=U$ . Essentially removes Hartree term in DMFT self energy—fixes p-d energy difference at band theory value. **No reason to choose  $U'=U$**

Phys. Rev. B89 161113 (2014)

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# LaTiO<sub>3</sub>: Full charge sc +FLL double counting produces metal even for large U

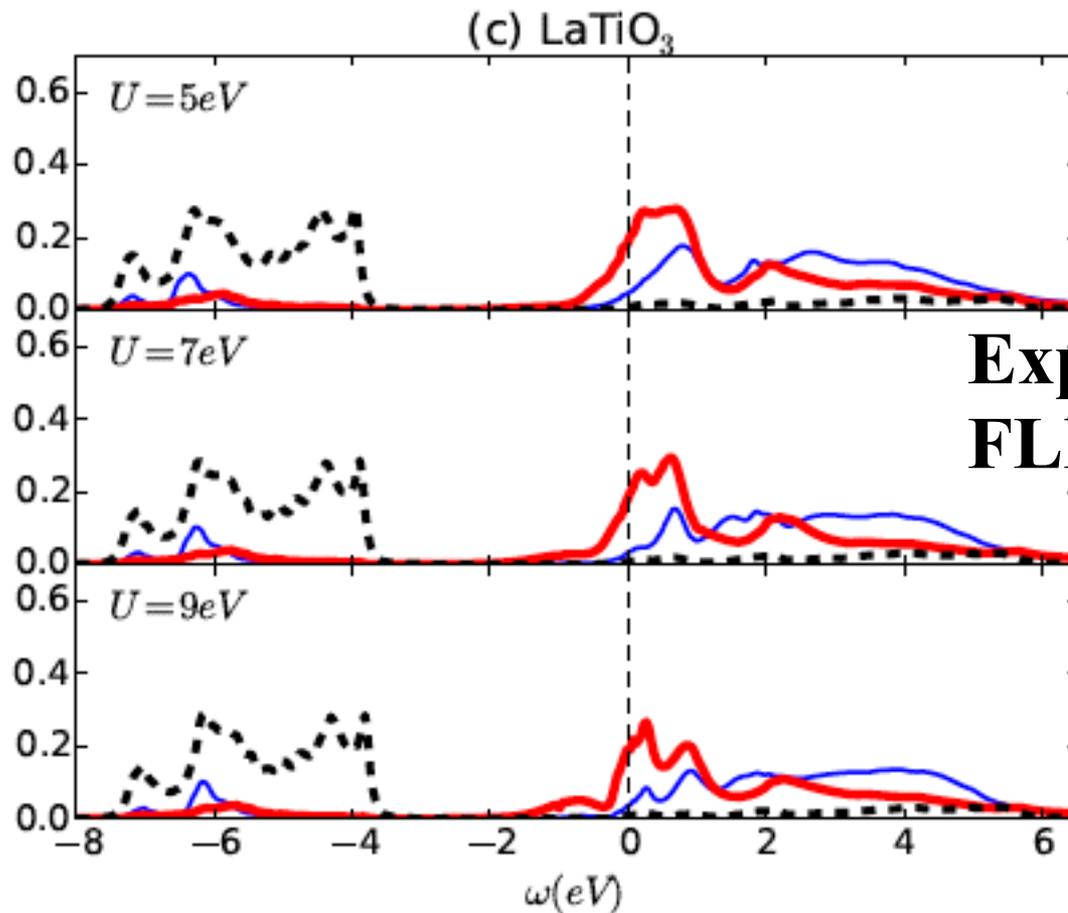


Experimental structure

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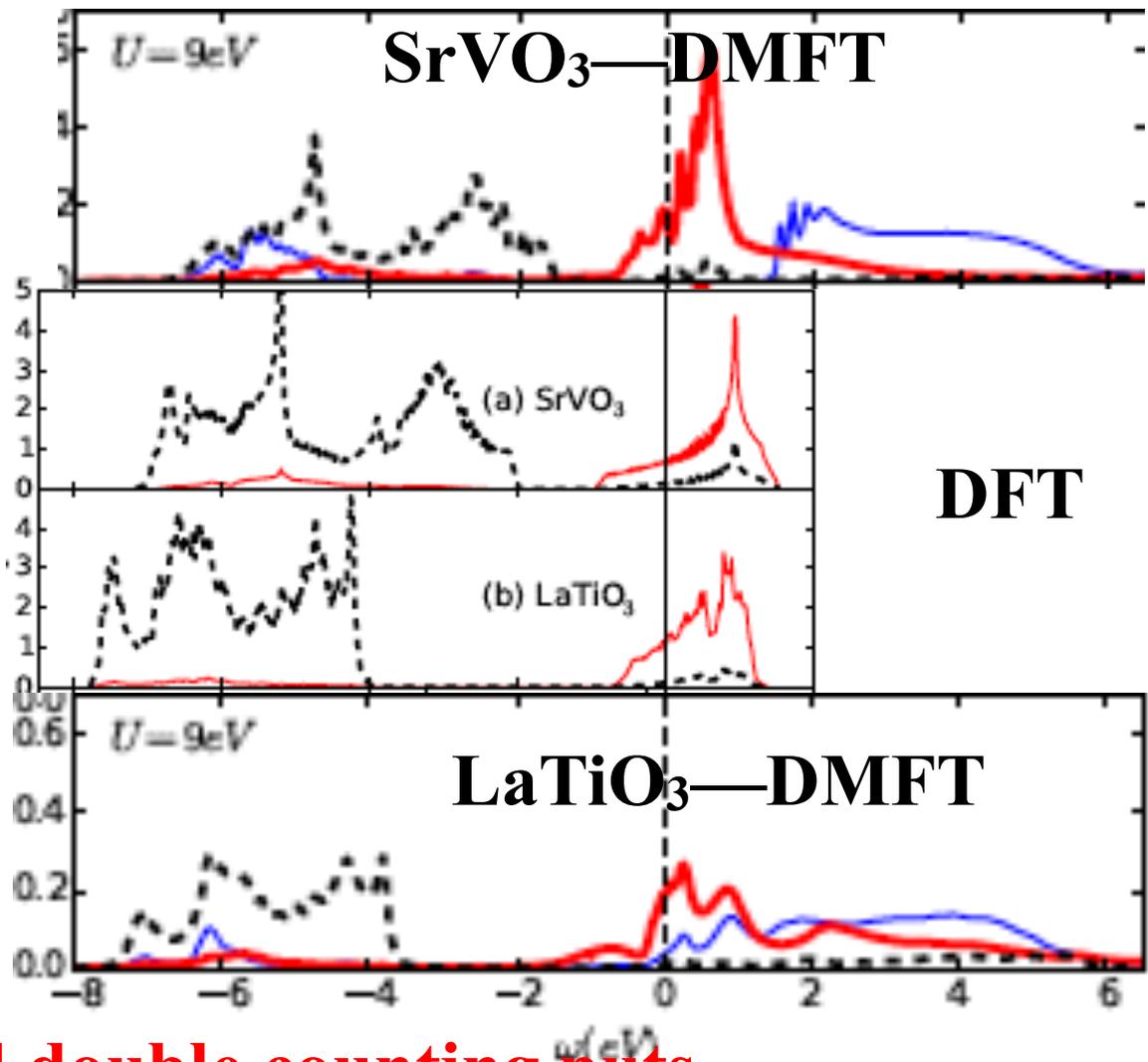
# At Fixed Double Counting: Charge transfer energy is indep of U



**Expt Structure**  
**FLL Double Counting**

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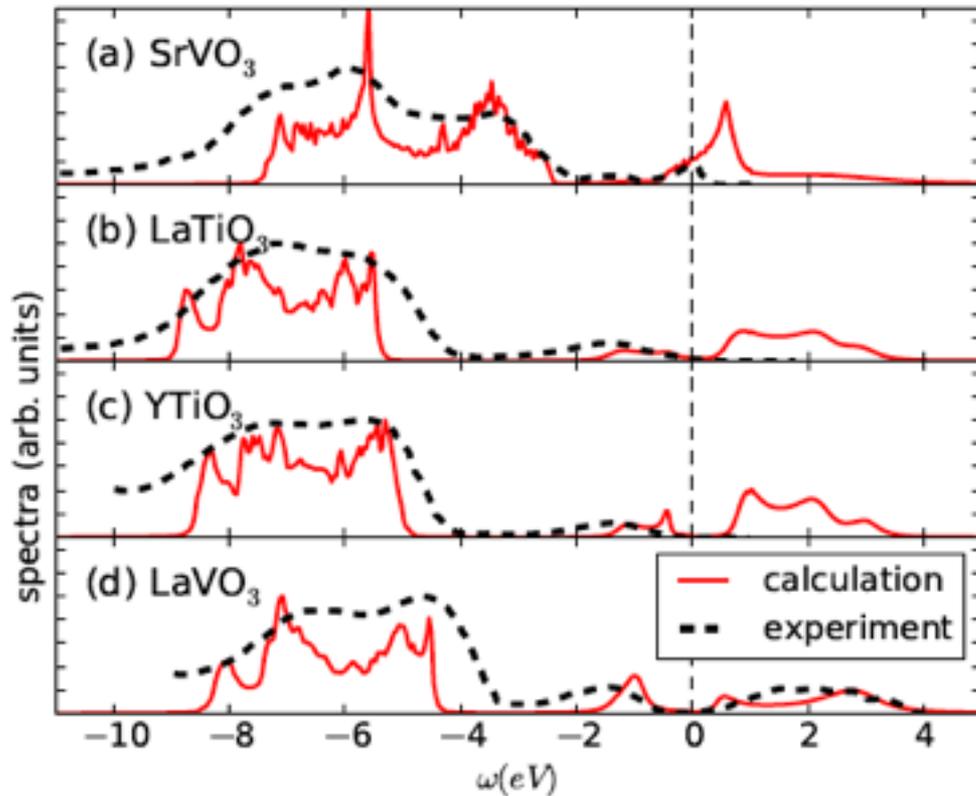
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**Standard double counting puts  
O2p at DFT position**

to get correct physics:  
adjust p-d energy splitting

$$V_{\text{DC}} = U' \langle N_d \rangle - \frac{5}{2} J \langle N_d \rangle$$



$U=5\text{eV}, J=0.65\text{eV}$

expt structures

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# Summary: DFT+DMFT

- Many-body treatment crucial for energetics of hybridization in correlated environment
- Charge self-consistency: crucial for 'embedding' (allowing background degrees of freedom to adjust to configuration of correlated site)
- Numerically exact solutions restricted to cases where correlated ion has not too low point symmetry
- **Uncertainties:**
  - formulation of many-body problem (what are the correlated orbitals and interactions)
  - the double-counting correction
  - values of beyond DFT interactions (' $U, J$ ')
  - adequacy of solution of many body problem (is single-site DMFT good enough)
  - **DONT** build a theory on spin-dependent functionals

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