

# EMBEDDED DYNAMICAL MEAN FIELD THEORY FUNCTIONAL (EDMFT)

*Kristjan Haule*

<http://hauleweb.rutgers.edu/tutorials/>

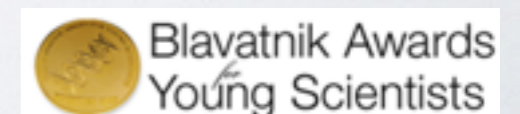
Home What is? Install Overview CTQMC MnO FeSe

## DFT + Embedded DMFT Functional\*

Developed by Kristjan Haule at Rutgers University, ©Copyright 2007-2017.



Support:



# PART 1 EDMFT

---

- What is DMFT, and DFT+embedded Dynamical Mean Field Theory
- How local are correlations in specific models?
- Projectors and applicability of local of correlations.

**Rev. Mod. Phys. 78, 865 (2006)**

G. Kotliar, S.Y. Savrasov, K Haule, V. S. Oudovenko, O. Parcollet, and C. A. Marianetti.

**Phys. Rev. B 81, 195107 (2010)**, K. Haule, Chuck-Hou Yee, Kyoo Kim.

# PART 2 EDMFT

---

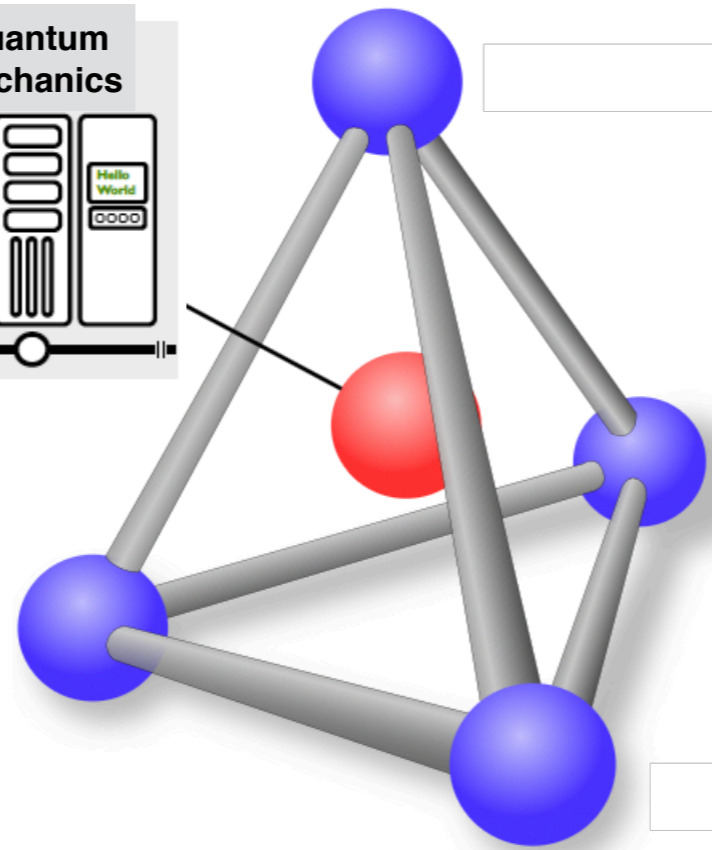
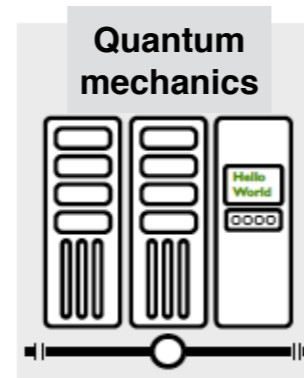
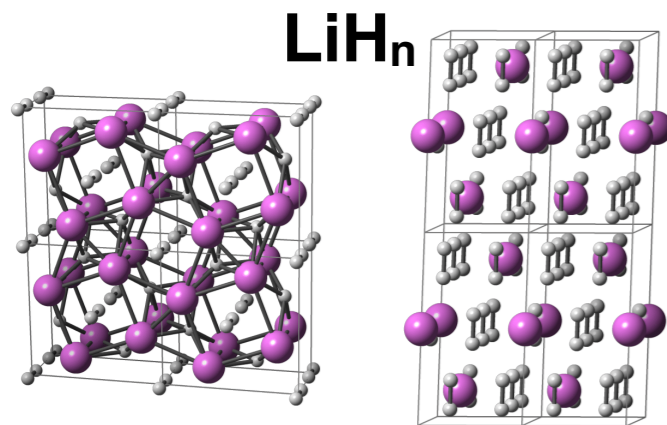
- *Exact double-counting of DFT+EDMFTF (PRL 115, 196403 (2015)).*
- *Stationary free energy functional (within Embedded DMFT approach) for structural optimization, PRL 115, 256402 (2015).*
- Implementation of Forces within eDMFT functional for optimization of internal structural parameter, (**Phys. Rev. B 49, 195146 (2016)**, K. Haule, G.L. Pascut)

# Modern material design workflow

## solve the inverse problem:

Given the functionality, what is the best material?

Constituent atoms (chemical formula)  
in a large unit cell



What is most likely  
crystal structure?

Is compound stable?  
(phonons stable,  
energy comparison with  
competing phases, is below  
the convex hull)

What are its properties?

*DFT made this possible for many classes of materials with weak interactions.*

# What made this theoretical revolution possible ?

**Basic laws of Physics S.E.**

$$E\psi(r) = -\frac{\hbar^2}{2m}\nabla^2\psi(r) + V(r)\psi(r)$$

DFT : Efficient method to solve  
Schroedinger Eq. reasonably well

*Development of methods to predict  
crystal structures from first principles*

*Development of methods to predict useful properties  
(electron-phonon coupling, phonon frequencies)*

*Fast computers*



*(BCS theory and Elliashberg theory existed for 60 years)*

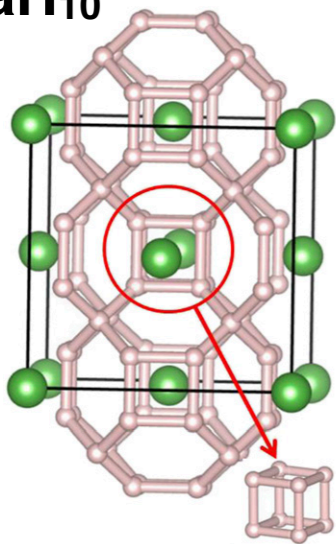
# Remarkable success of DFT in hydrides

Thorough search of many hydrides (DFT) :  $\text{LaH}_{10}$  and  $\text{YH}_{10}$  stand out in  $T_c$ .  
(many groups)

H. Liu, I. I. Naumov, R. Hoffmann, N.W.Ashcroft, and R. J. Hemley,  
PNAS 27, 6990-6995 (2017).

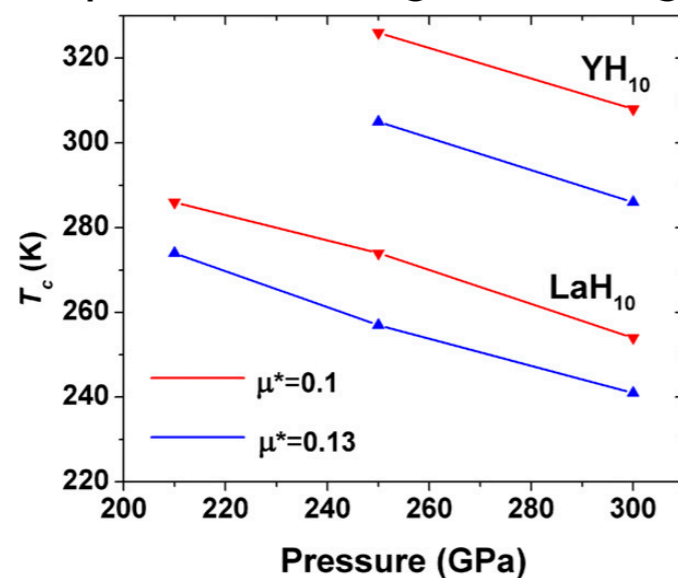
Eva Zurek et.al., arXiv 1806.00163

$\text{LaH}_{10}$

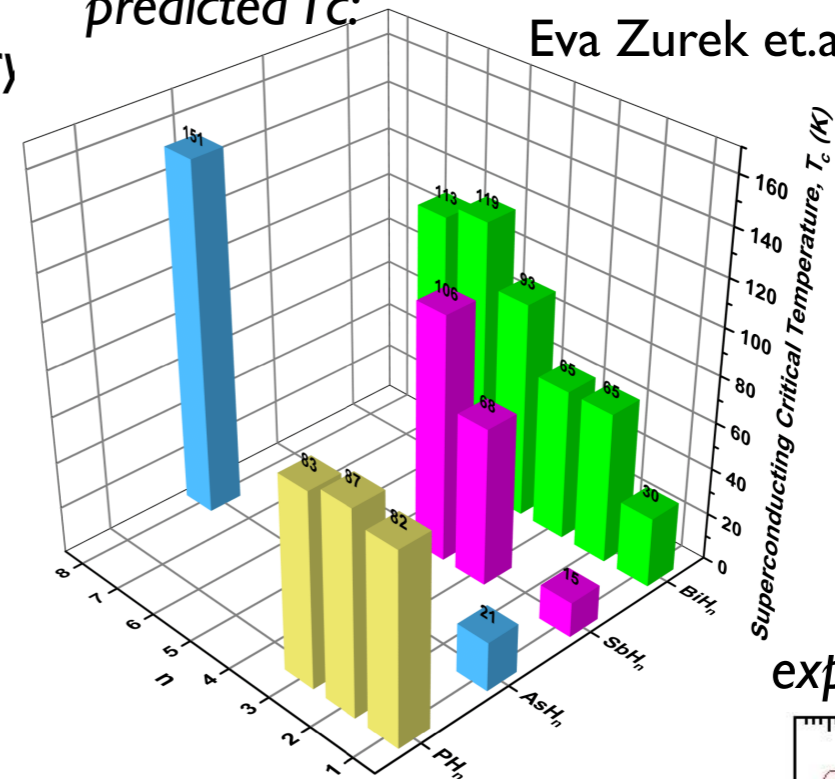


correct prediction of crystal structure is crucial, made revolution possible

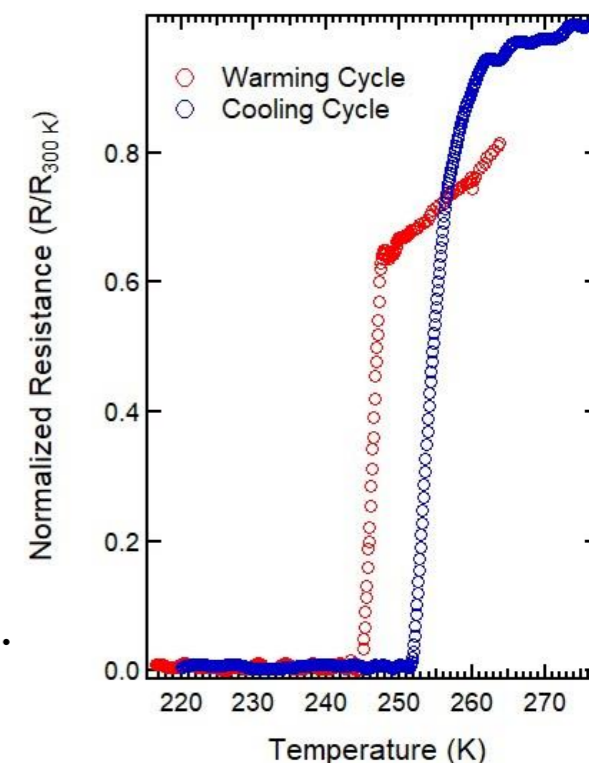
$T_c$  prediction using Eliashberg Theory



predicted  $T_c$ :



experiment resistivity:



Experimentally confirmed by two groups :

$\text{LaH}_{10}$  @ 170GPa with  $T_c=250\text{K}$

A. P. Drozdov, M. I. Erements, arXiv 1808.07039; *Nature* **569**, 528–531 (2019).

$\text{LaH}_{10}$  @ 190GPa with  $T_c=260\text{K}$

M. Somayazulu, ..., J. Hemley et.al., arXiv 1808.07695; *PRL* **122**, 027001 (2019).

# All existing materials in databases (materials genome)

<https://materialsproject.org>

The screenshot shows the Materials Project website interface. At the top, there is a search bar with the text "by Formula" and "VO2" entered. Below the search bar is a periodic table of elements. A red oval highlights the transition metal elements (groups 3-10) and the lanthanide and actinide series. Below the periodic table, there is a table of materials with columns for Materials Id, Formula, Spacegroup, Formation Energy (eV), E Above Hull (eV), Band Gap (eV), Volume, Nsites, and Density (gm/cc). The table lists several materials, including VO2, La2CuO4, Sr2IrO4, SrVO3, and FeO.

Materials Id	Formula	Spacegroup	Formation Energy (eV)	E Above Hull (eV)	Band Gap (eV)	Volume	Nsites	Density (gm/cc)
mp-19094	VO <sub>2</sub>	P4 <sub>2</sub> /mnm	-2.484	0	0.984	247.552	24	4.451
mp-1077929	La <sub>2</sub> CuO <sub>4</sub>	I4/mmm	-3.053	0	0.000	101.516	7	6.631
mp-4998	Sr <sub>2</sub> IrO <sub>4</sub>	I4 <sub>1</sub> /acd	-2.374	0	0.000	400.36	28	7.158
mp-18717	SrVO <sub>3</sub>	Pm $\bar{3}$ m	-2.892	0.036	0.245	59.36	5	5.219
mp-18905	FeO	Fm $\bar{3}$ m	-1.256	0.414	0.000	20.112	2	5.932

Active d/f shell materials :  
DFT will likely fail

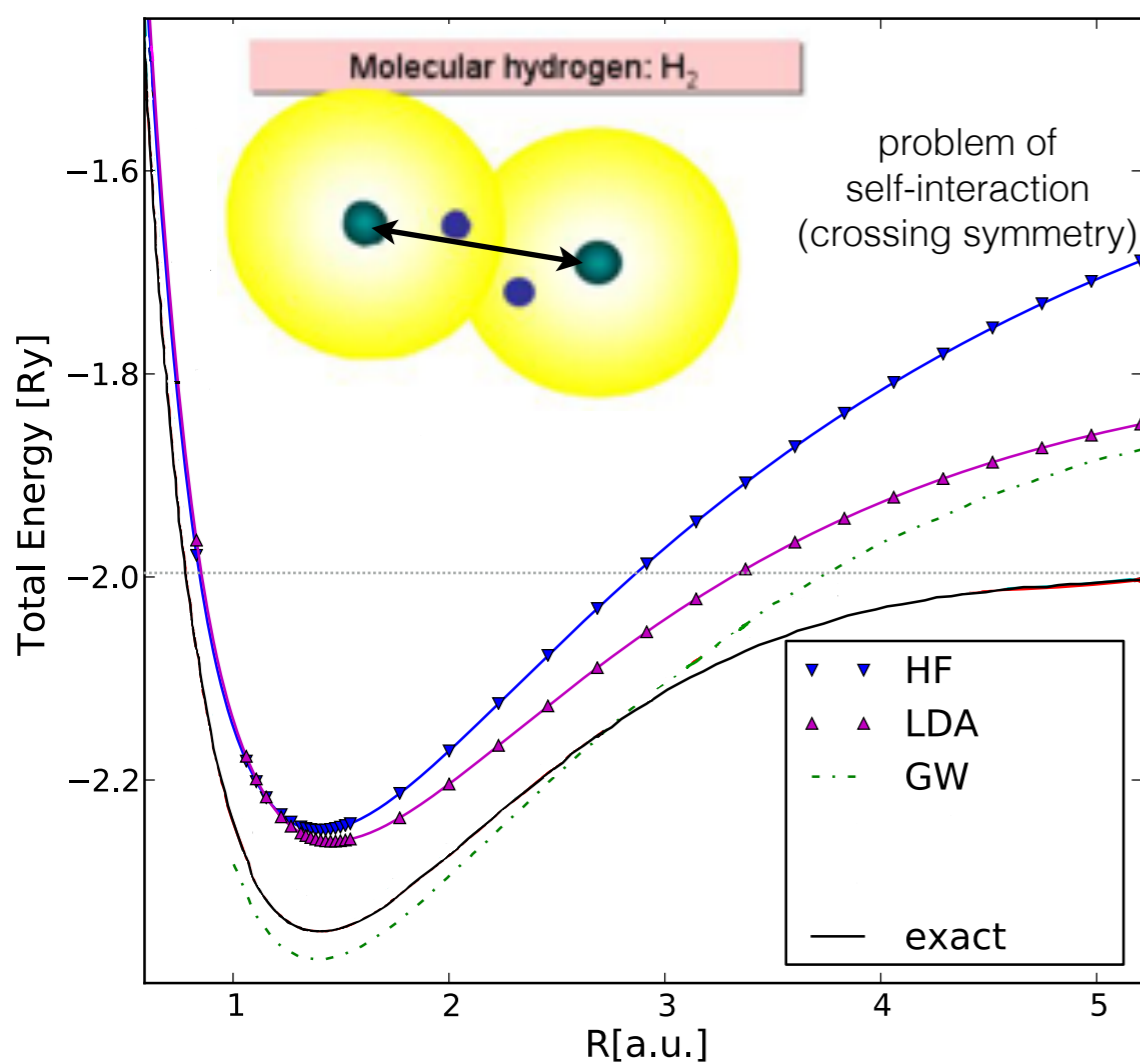
**Experiment:**  
rutile VO<sub>2</sub>, metal  
La<sub>2</sub>CuO<sub>4</sub>, Mott insulator  
Sr<sub>2</sub>IrO<sub>4</sub>, Mott insulator  
SrVO<sub>3</sub>, metal  
FeO rocksalt, Mott insulator

# Many challenges remain: new generation of physicist needed

Archetypal problem of strong correlations:

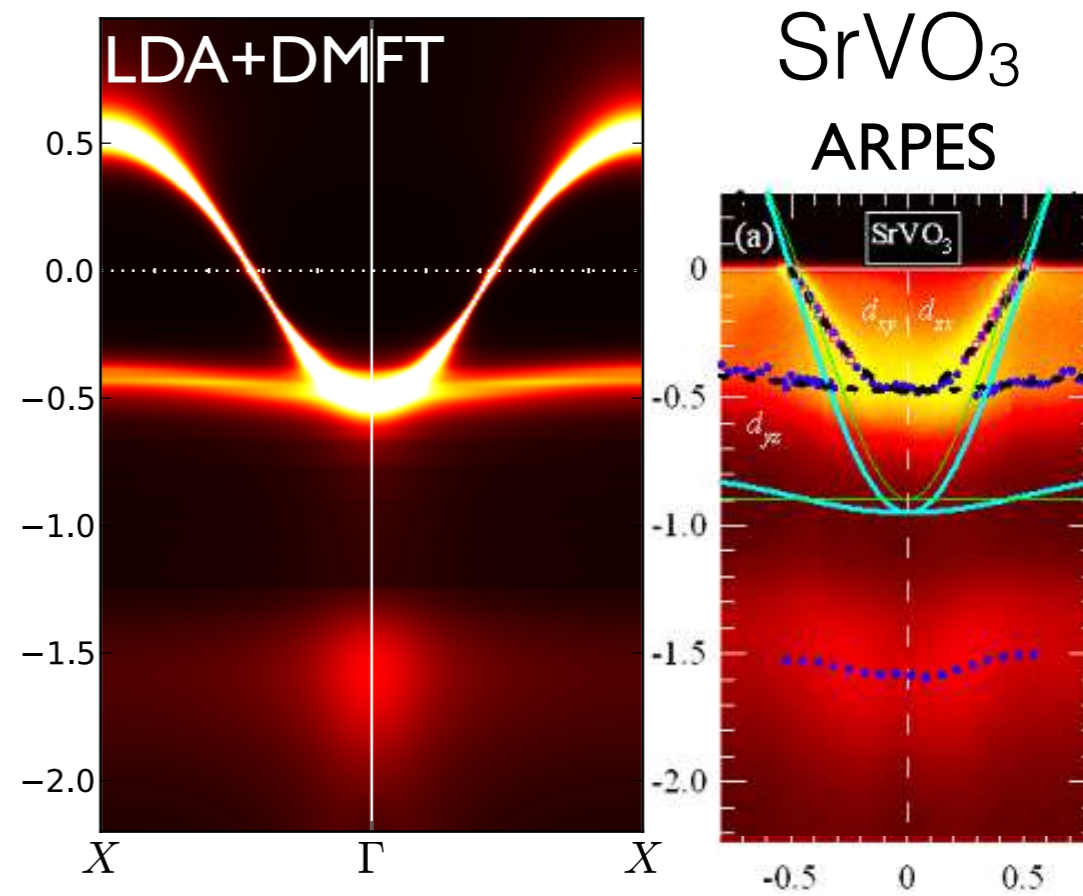
## H2 molecule

$$\langle n_{\uparrow\mathbf{R}} n_{\downarrow\mathbf{R}} \rangle = 0 \neq \langle n_{\uparrow\mathbf{R}} \rangle \langle n_{\downarrow\mathbf{R}} \rangle = 1/4$$



correct eq. distance,  
but not great energy

Excited states often challenging  
even in moderately interacting solids



band narrowing in metals  
gap underestimation in semiconductors

$$G_0W_0 = \frac{1}{2} \left[ \text{self-energy diagram 1} \right] + \frac{1}{2} \left[ \text{self-energy diagram 2} \right] + \frac{1}{4} \left[ \text{self-energy diagram 3} \right] + \frac{1}{3} \left[ \text{self-energy diagram 4} \right] + \dots + \frac{1}{6} \left[ \text{self-energy diagram 5} \right] + \dots$$

# Indirect approach through functionals

## Density Functional Theory:

- Is the workhorse of the theoretical material science
- It relates some aspects of the solution of real problem to solution of a more tractable auxiliary problem (electron gas + system of independent fermions)
- Even purely local exchange-correlation, i.e., LDA/GGA (subject to mean-field type self-consistency) gives total energy and charge density surprisingly well (but can fail in strongly correlated systems)

Extremizing a functional of electron density  $\rho$  to obtain **ground state** energy and electron density  $\rho$ :

$$E[\{\rho(\mathbf{r})\}] = \underbrace{E_{kin}[\{\rho\}] + E_{int}[\{\rho\}]}_{\substack{\text{universal functional} \\ \text{independent of material} \\ \text{depends on EM interaction}}} + \int d\mathbf{r} V_{ext}(\mathbf{r})\rho(\mathbf{r})$$

material dependent term

$$E_{int}[\{\rho\}] = E_H[\{\rho\}] + E_{XC}[\{\rho\}]$$

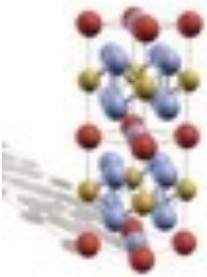
LDA-XC:  $E_{XC}^{LDA}[\{\rho\}] = \int d\mathbf{r} \rho(\mathbf{r}) \epsilon_{V_C}^{XC}(\rho(\mathbf{r}))$

Kohn & Sham (1965): To minimize the functional:

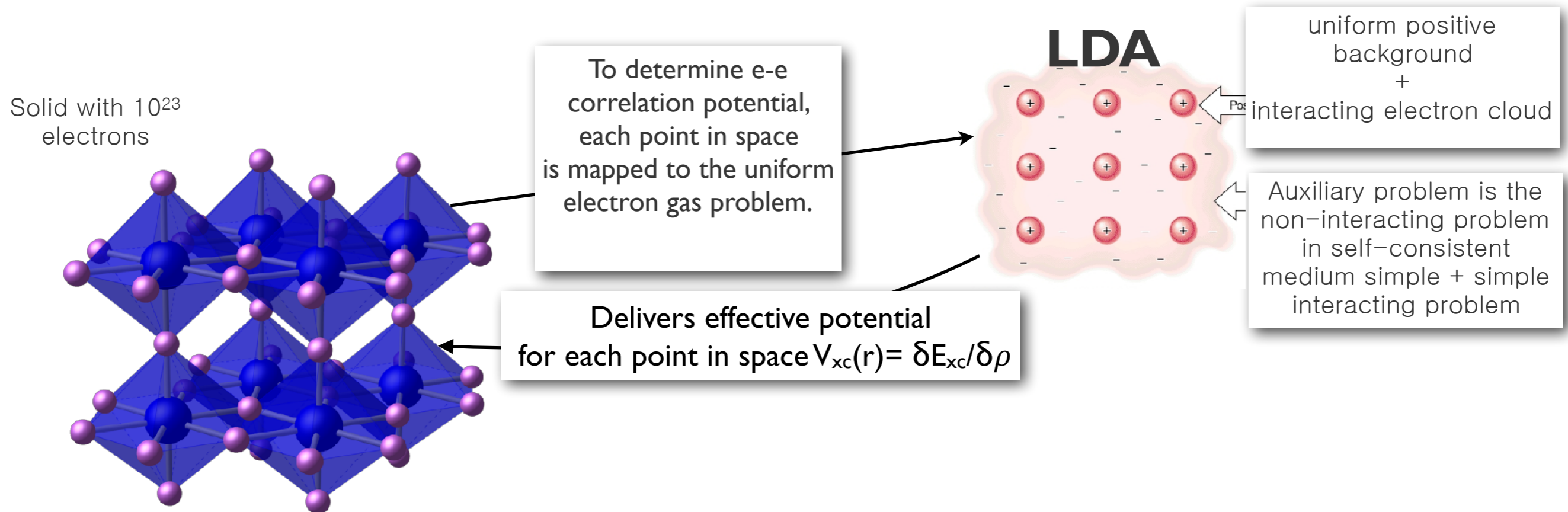
solve auxiliary single-particle problem + self-consistency condition



# Practical solution of DFT equations

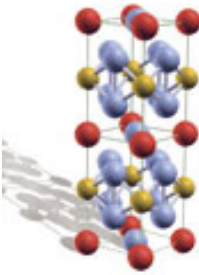


LDA: Accounts for exchange-correlations local to a given point in space. Different points in space are coupled through kinetic energy and Hartree term.



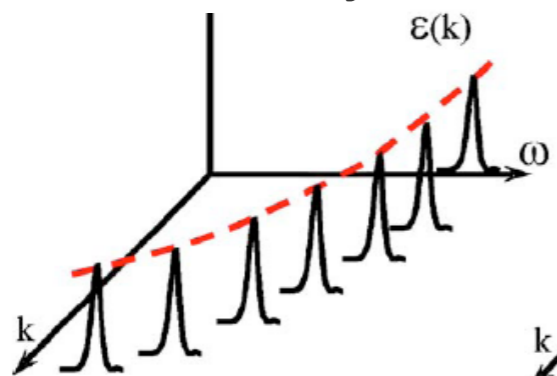
Dyson equation is solved for all electrons in the problem.

# Theoretical Perspective - Correlates Matter

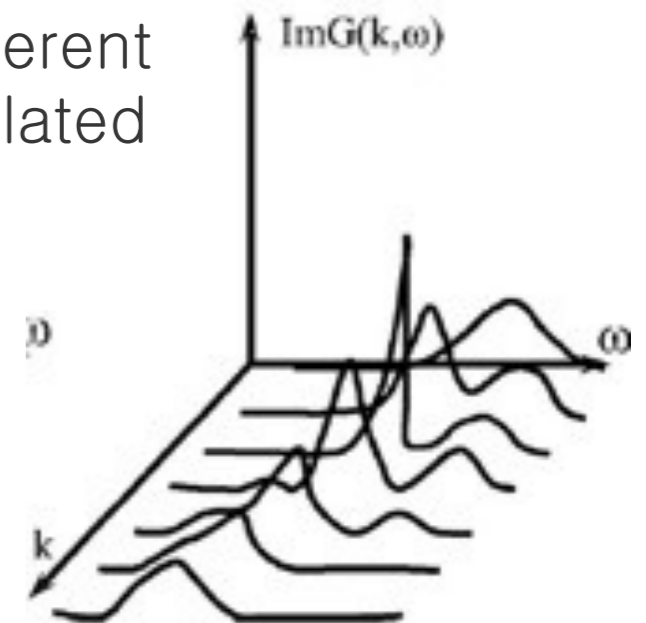


- In correlated solids, electrons have dual nature, i.e., partly itinerant and partly localized, and can not be described in terms of an auxiliary non-interacting system (**bands are not well defined**)  $\langle n_{\uparrow\mathbf{R}} n_{\downarrow\mathbf{R}} \rangle \approx 0 \neq \langle n_{\uparrow\mathbf{R}} \rangle \langle n_{\downarrow\mathbf{R}} \rangle = 1/4$
- In  $\text{H}_2$  molecule, the two electrons remain entangled (in mean-field basis) for any separation. In atomic basis they are entangled at any finite separation.
- Reducing double-occupancy leads to narrowing of bands in metals, and ultimately to Mott physics at large interaction.
- Need to properly treat (by beyond mean field) Hubbard interaction (Mottness), Hund's interaction (orbital differentiation, and Hund's metallicity) and orbital physics,.

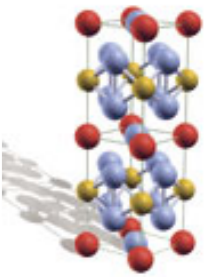
Rigid band picture in standard theory



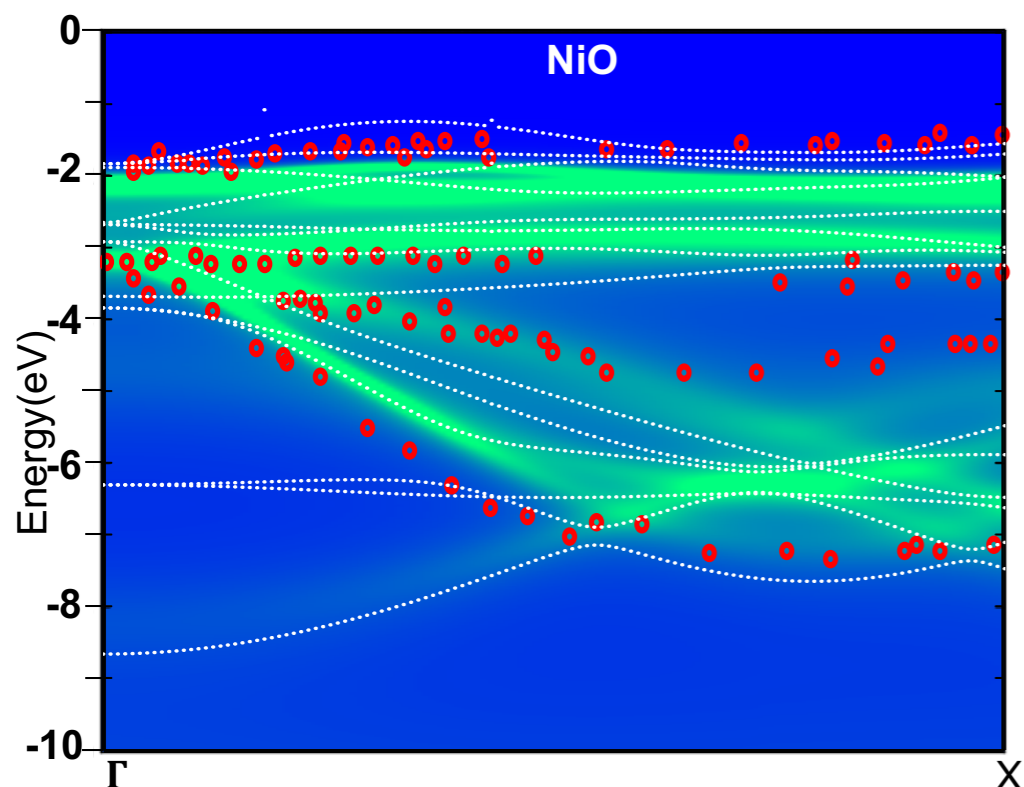
Coherent+incoherent spectra in correlated materials



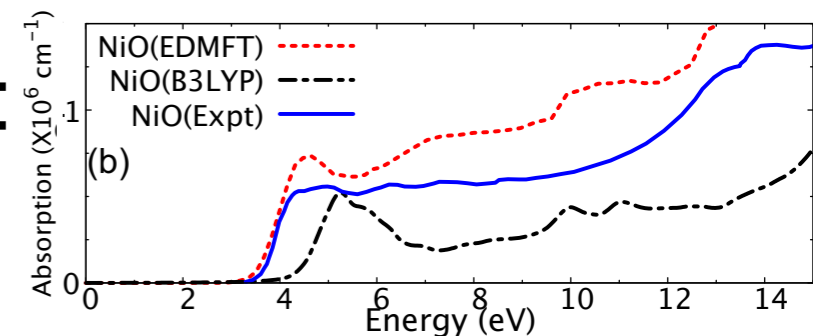
# Theoretical Perspective - Correlates Matter



- In correlated solids, electrons have dual nature, i.e., partly itinerant and partly localized, and can not be described in terms of an auxiliary non-interacting system (**bands are not well defined**)  $\langle n_{\uparrow\mathbf{R}} n_{\downarrow\mathbf{R}} \rangle \approx 0 \neq \langle n_{\uparrow\mathbf{R}} \rangle \langle n_{\downarrow\mathbf{R}} \rangle = 1/4$
- In  $\text{H}_2$  molecule, the two electrons remain entangled (in mean-field basis) for any separation. In atomic basis they are entangled at any finite separation.
- Reducing double-occupancy leads to narrowing of bands in metals, and ultimately to Mott physics at large interaction.
- Need to properly treat (by beyond mean field) Hubbard interaction (Mottness), Hund's interaction (orbital differentiation, and Hund's metallicity) and orbital physics,.



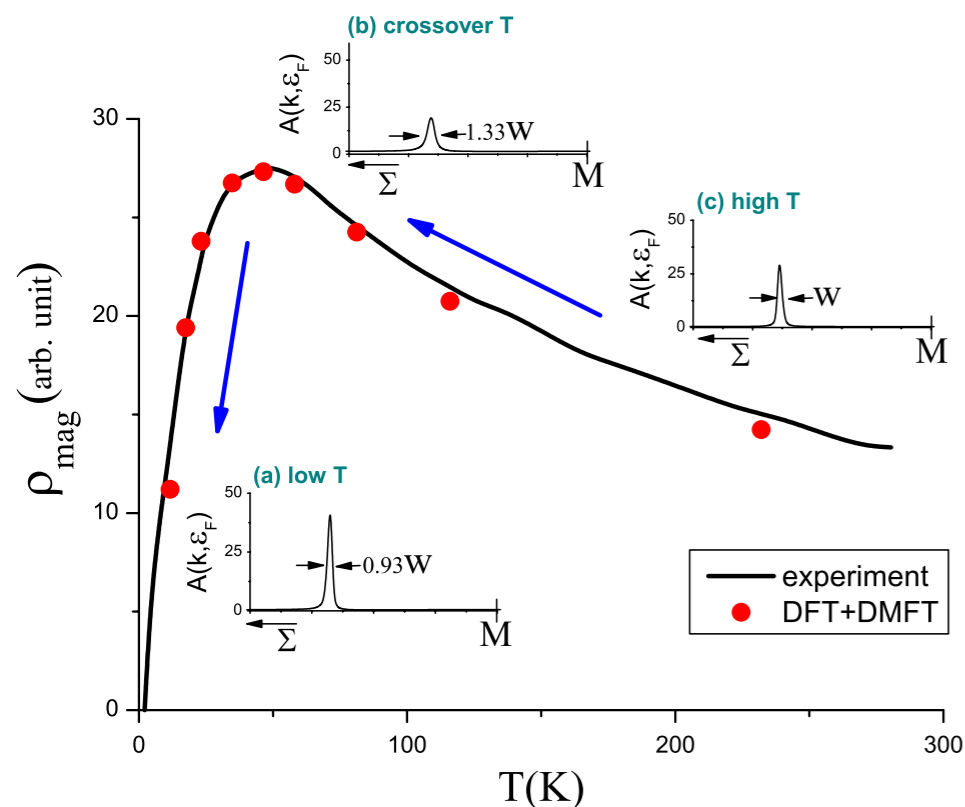
Example on NiO:  
red circles: ARPES  
white lines: B3LYB  
green spectra: DFT+eDMFT



Rigid band picture in static theories (including B3LYB) replaced by coherent+incoherent spectra

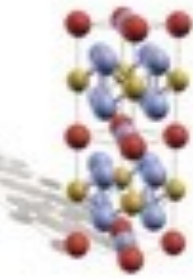
# Theoretical Perspective - Correlates Matter

- In correlated solids, electrons have dual nature, i.e., partly itinerant and partly localized, and can not be described in terms of an auxiliary non-interacting system (**bands are not well defined**)  $\langle n_{\uparrow\mathbf{R}}n_{\downarrow\mathbf{R}} \rangle \approx 0 \neq \langle n_{\uparrow\mathbf{R}} \rangle \langle n_{\downarrow\mathbf{R}} \rangle = 1/4$
- In  $H_2$  molecule, the two electrons remain entangled (in mean-field basis) for any separation. In atomic basis they are entangled at any finite separation.
- Reducing double-occupancy leads to narrowing of bands in metals, and ultimately to Mott physics at large interaction.
- Need to properly treat (by beyond mean field) Hubbard interaction (Mottness), Hund's interaction (orbital differentiation, and Hund's metallicity) and orbital physics,.



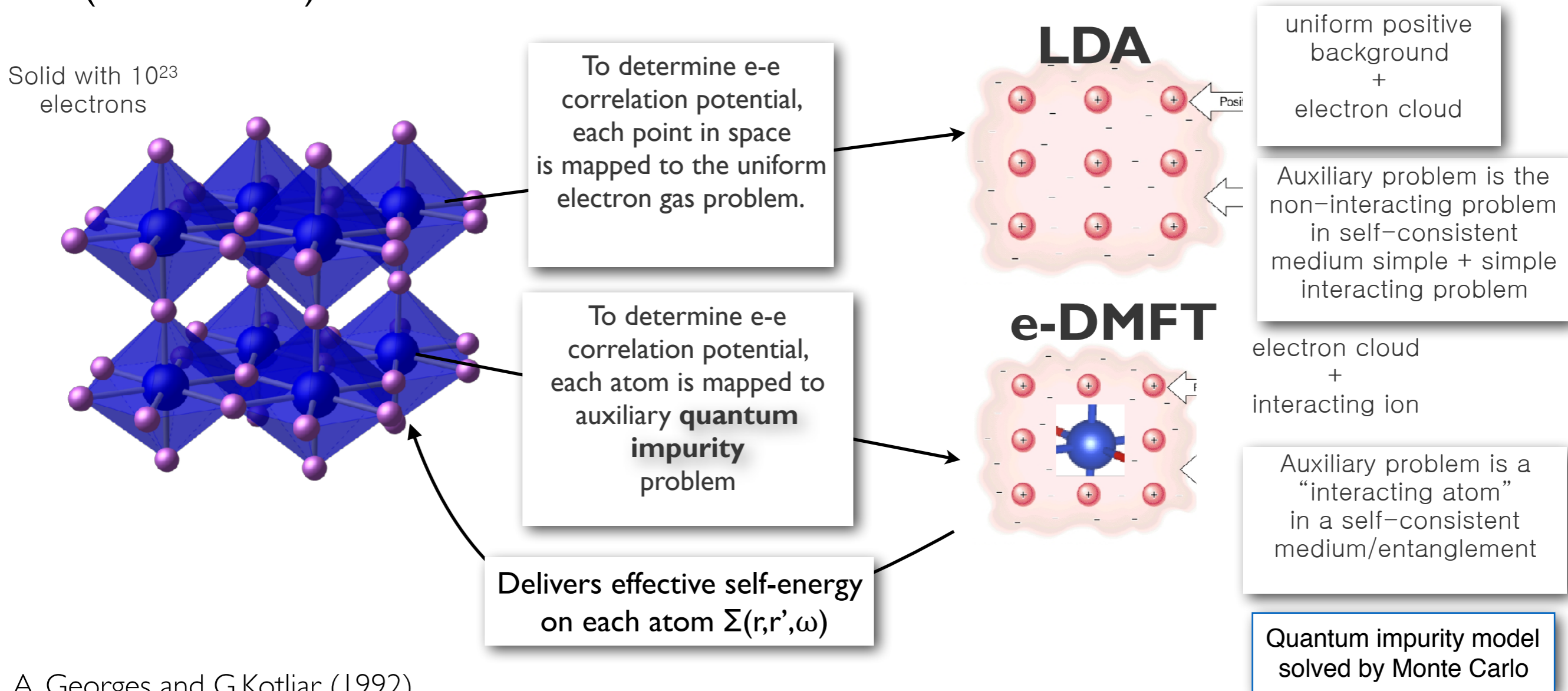
Example resistivity of CeIrIn5:  
 red circles: DFT+eDMFT  
 black line: resistivity of  $\rho(\text{CeIrIn5}) - \rho(\text{LaIrIn5})$

# DFT+embedded Dynamical Mean Field Theory



**LDA:**Accounts for exchange-correlations local to a given point in space. Different points in space are coupled through kinetic energy and Hartree term.

**eDMFT:**Accounts for exchange-correlations on a given correlated ion ( or a cluster of ions ) exactly, including retardation effects. The inter-cluster degrees of freedom treated on the mean-field (Hartree level).

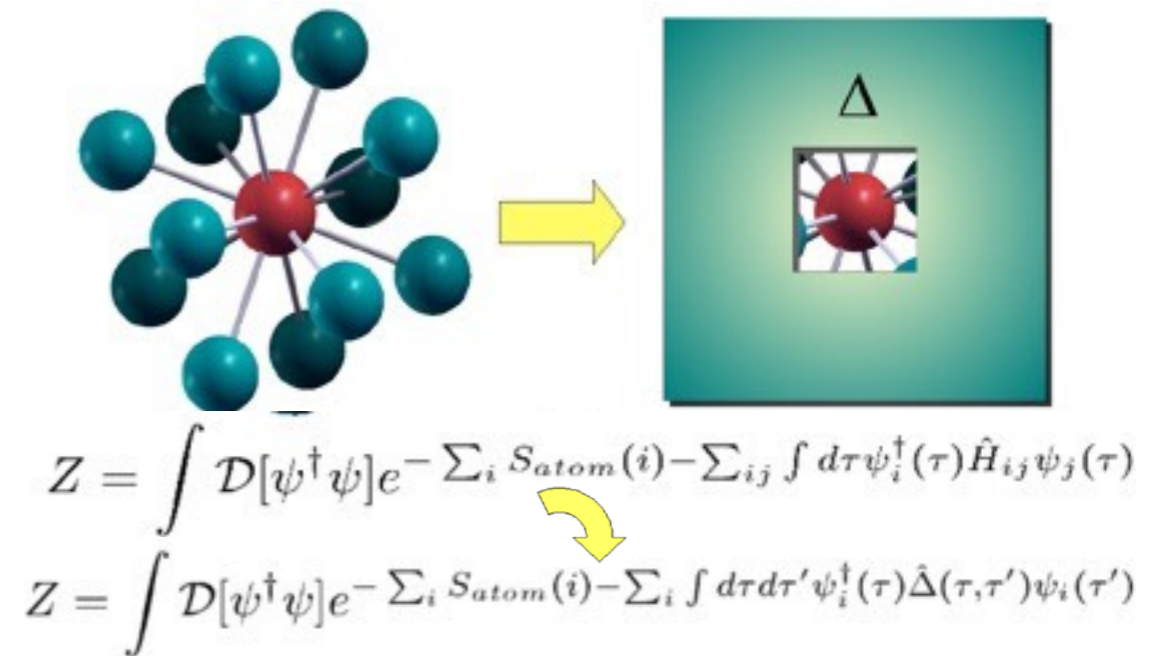
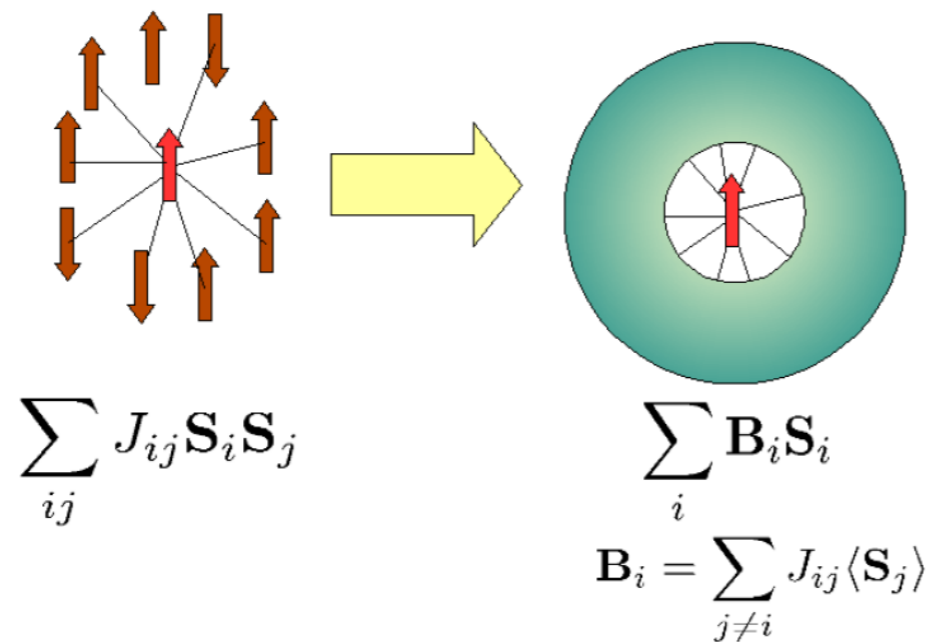


A. Georges and G.Kotliar (1992)

Dyson equation is solved for all electrons in the problem both in DFT and DFT+eDMFT

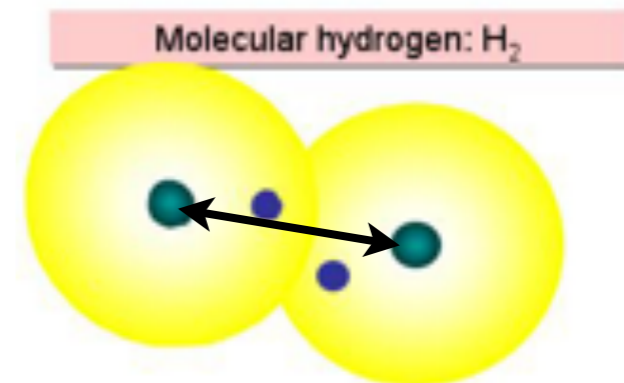
# How local are correlations?

Correlations are local in large  $d$  (large connectivity  $z$ ) where DMFT is exact -- Weiss mean field theory



What about finite  $D$ ? What about  $0$ ?

H<sub>2</sub> molecule:

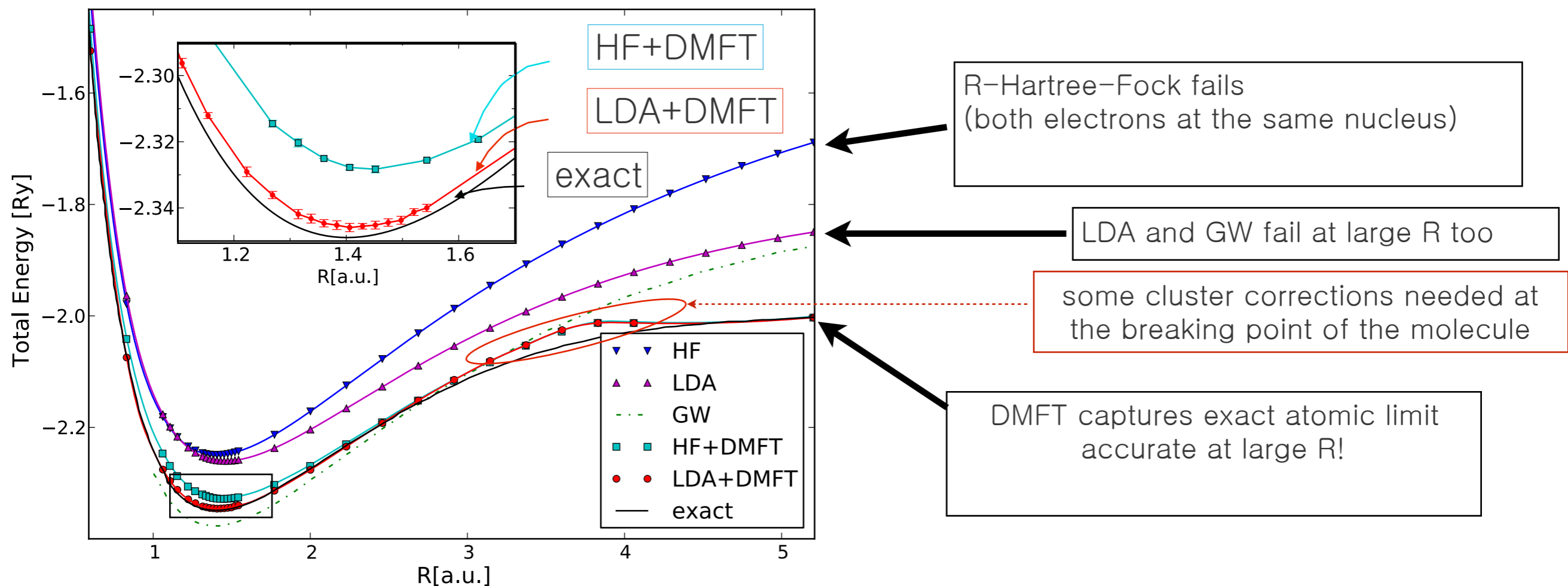
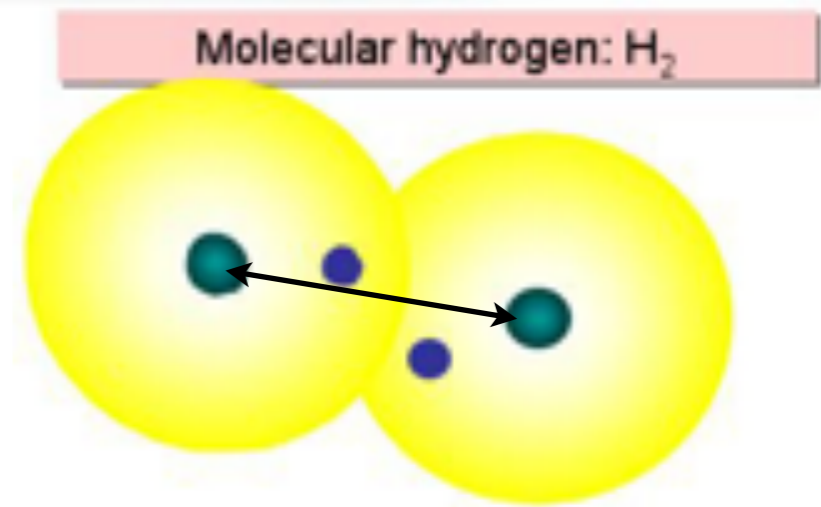


# How local are correlations in real space? 0-D test of the single site DMFT.

Archetypal problem of strong correlations:

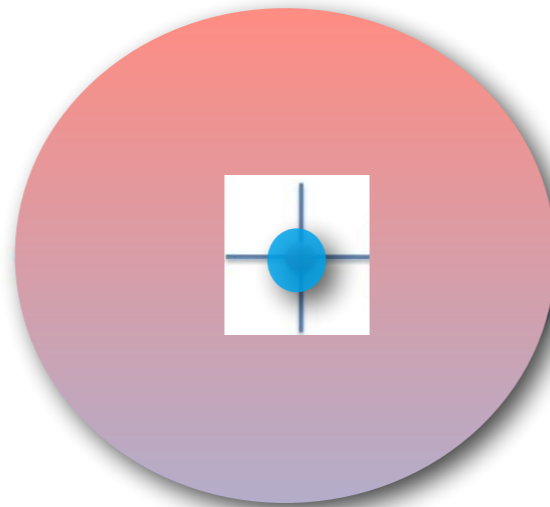
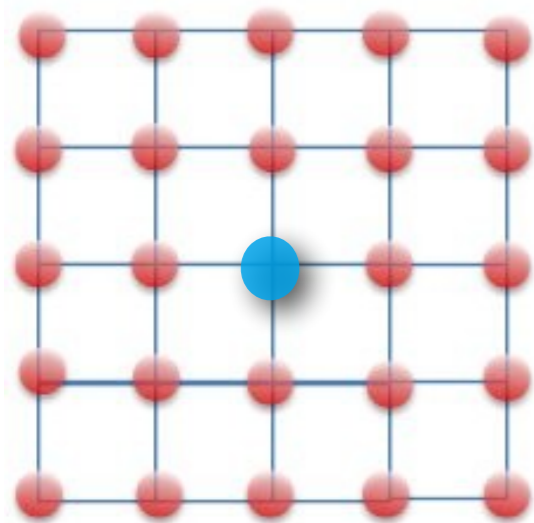
**DMFT exact in  $\infty$  D**, or large connectivity Z

It is not expected to be good for low-D problems  
(like H<sub>2</sub> molecule)

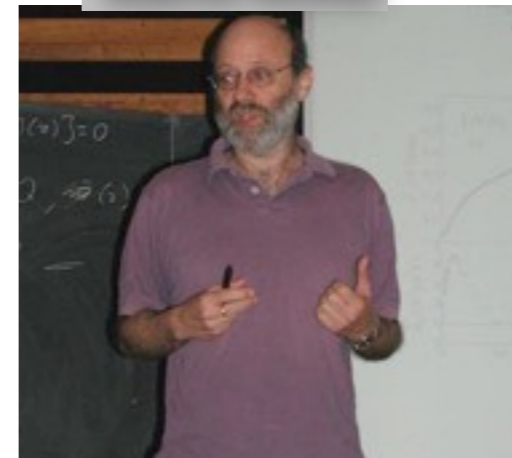


# DYNAMICAL MEAN FIELD

First introduced in the context of lattice models (Hubbard model) to describe Mott transition



Gabriel Kotliar



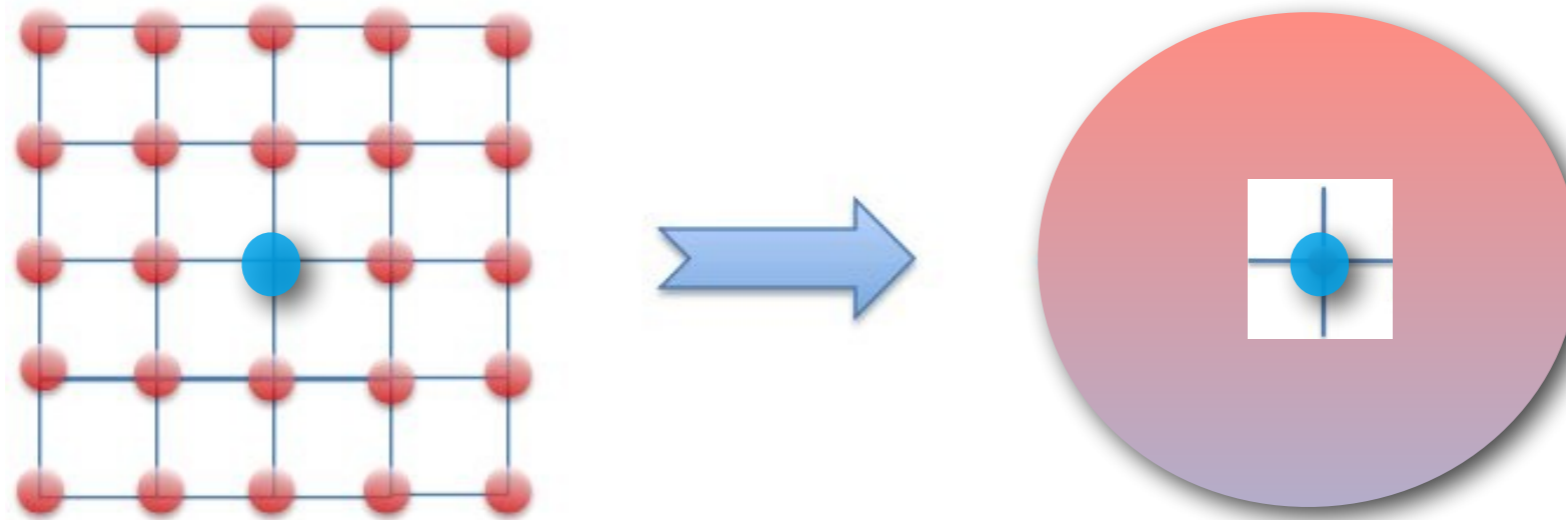
Antoine Georges



local correlations on a given site can be computed **exactly** by solving a quantum impurity model



# DMFT THROUGH WEISS FIELD



$$(G_{ii} \ U_{ii} ; \Sigma_{ii}) = (G_{imp} \ U_{imp} ; \Sigma_{imp})$$

Like the self-consistency on the B-field in spin system, in DMFT the requirement is

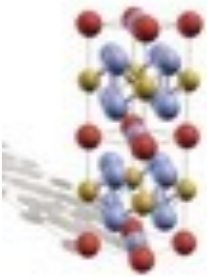
$$G_{imp} = G_{ii} \quad \text{and} \quad \Sigma_{ii} = \Sigma_{imp}$$

$$\mathbf{B}_i = \sum_{j \neq i} J_{ij} \langle \mathbf{S}_j \rangle$$

In the Hubbard model this lead to familiar DMFT SCC:

$$\sum_{\mathbf{k}} (i\omega + \mu - \varepsilon_{\mathbf{k}} - \Sigma_{ii})^{-1} = (i\omega - E_{imp} - \Delta - \Sigma_{ii})^{-1}$$

# Functional point of view



Basic variable is Green's function:

== dynamic analog of charge density

$$G(\mathbf{r}\tau, \mathbf{r}'\tau') = \langle T_\tau \psi^\dagger(\mathbf{r}'\tau') \psi(\mathbf{r}, \tau) \rangle \quad \rho(\mathbf{r}) = G(\mathbf{r}\tau, \mathbf{r}\tau)$$

Luttinger–Ward functional gives electronic free energy:

$$\Gamma[\{G\}] = \underbrace{-\text{Tr}((G_0^{-1} - G^{-1})G)}_{\text{material dependent term}} + \underbrace{\text{Tr} \log(-G) + \Phi[\{G\}]}_{\text{universal functional independent of material expressible by the perturbation theory}}$$

$$G_0^{-1}(\mathbf{r}, \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}') \left[ \omega + \mu + \frac{\nabla^2}{2m} - V_{nuc}(\mathbf{r}) \right]$$

$\Phi[G]$  *Is a sum of all connected two particle irreducible Feynman diagrams (skeleton diagrams).*

$$\Phi[G] = \frac{1}{2} \text{diagram 1} + \frac{1}{2} \text{diagram 2} + \frac{1}{4} \text{diagram 3} + \dots$$

legend:  $\longrightarrow G$   
 $\cdots v_c(\mathbf{r} - \mathbf{r}') = \frac{1}{|\mathbf{r} - \mathbf{r}'|}$

# Functional point of view

DMFT for lattice models:

$$\Phi[\{G_{ij}\}] \rightarrow \sum_i \Phi[\{G_{ii}\}] \quad i \text{ is site or cluster}$$

$\longrightarrow$   $G$   
 $\cdots$   $v_c(\mathbf{r} - \mathbf{r}') = \frac{1}{|\mathbf{r} - \mathbf{r}'|}$  or  $U_{ijklk}$

compare:  $\Phi^{XC}[\{\rho\}] = \int \phi^{LDA}(\rho(\mathbf{r})) d\mathbf{r}$

$$\Phi^{exact}[G] = \frac{1}{2} \begin{array}{c} \circlearrowleft \\ \vdots \\ \circlearrowright \end{array} + \frac{1}{2} \begin{array}{c} \circlearrowleft \\ \text{---} \\ \circlearrowright \end{array} + \frac{1}{4} \begin{array}{c} \circlearrowleft \\ \text{---} \\ \circlearrowleft \\ \text{---} \\ \circlearrowright \end{array} + \dots + \frac{1}{6} \begin{array}{c} \circlearrowleft \\ \text{---} \\ \circlearrowleft \\ \text{---} \\ \circlearrowleft \\ \text{---} \\ \circlearrowright \end{array} + \dots$$

*Exact for the solid*

$$\Phi^{DMFT}[G] = \sum_i \frac{1}{2} \begin{array}{c} \circlearrowleft \\ \vdots \\ \circlearrowright \end{array} + \frac{1}{2} \begin{array}{c} \circlearrowleft \\ \text{---} \\ \circlearrowright \end{array} + \frac{1}{4} \begin{array}{c} \circlearrowleft \\ \text{---} \\ \circlearrowleft \\ \text{---} \\ \circlearrowright \end{array} + \dots + \frac{1}{6} \begin{array}{c} \circlearrowleft \\ \text{---} \\ \circlearrowleft \\ \text{---} \\ \circlearrowleft \\ \text{---} \\ \circlearrowright \end{array} + \dots$$

*DMFT approximation for the solid*

$$\Phi^{imp}[G_{imp}] = \frac{1}{2} \begin{array}{c} \circlearrowleft \\ \vdots \\ \circlearrowright \end{array} + \frac{1}{2} \begin{array}{c} \circlearrowleft \\ \text{---} \\ \circlearrowright \end{array} + \frac{1}{4} \begin{array}{c} \circlearrowleft \\ \text{---} \\ \circlearrowleft \\ \text{---} \\ \circlearrowright \end{array} + \dots + \frac{1}{6} \begin{array}{c} \circlearrowleft \\ \text{---} \\ \circlearrowleft \\ \text{---} \\ \circlearrowleft \\ \text{---} \\ \circlearrowright \end{array} + \dots$$

*Exact for impurity*

If we arrange  $G_{ii}^{lattice} = G_{imp}$  then  $\Sigma_{ii} = \frac{\delta \Phi^{DMFT}}{\delta G_{ii}} = \frac{\delta \Phi^{imp}}{\delta G_{imp}} = \Sigma_{imp}$

# Functional point of view

*Impurity solver is a trick to calculate the functional*

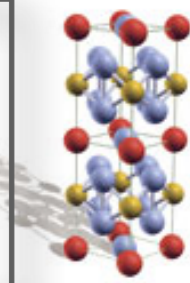
$$\Phi^{DMFT}[G]$$

$$\Phi^{imp}[G_{imp}] = \frac{1}{2} \begin{array}{c} \circlearrowleft i \\ \vdots \\ \circlearrowright i \end{array} + \frac{1}{2} \begin{array}{c} \circlearrowleft i \text{---} i \\ \circlearrowright \end{array} + \frac{1}{4} \begin{array}{c} \circlearrowleft i \text{---} i \\ \circlearrowright i \text{---} i \end{array} + \dots + \frac{1}{6} \begin{array}{c} \circlearrowleft i \text{---} i \\ \circlearrowright i \text{---} i \\ \circlearrowright i \text{---} i \end{array} + \dots$$

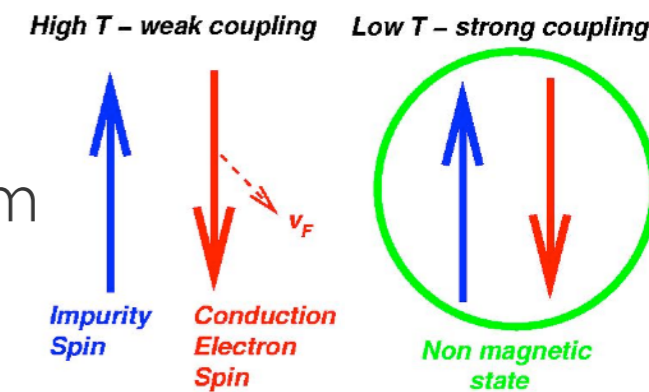
***Exact for impurity***

If we arrange  $G_{ii}^{lattice} = G_{imp}$  then  $\Sigma_{ii} = \frac{\delta \Phi^{DMFT}}{\delta G_{ii}} = \frac{\delta \Phi^{imp}}{\delta G_{imp}} = \Sigma_{imp}$

# At the heart of DMFT: Q.Imp.M.



**50+ year old problem : Anderson impurity** (Kondo) problem  
(Kondo, Jun (1964) )



Thermodynamics solved by Numerical Renormalization Group (Wilson, 1975).

Dynamics too slow for  $>3$  orbitals.

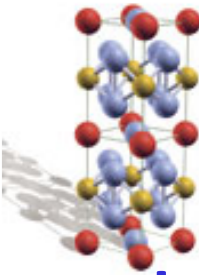
For constant bath and single band problem Bethe-Ansantz solution exists  
(Wiegmann, (1980), N. Andrei (1980)).

Not useful for DMFT -- strongly energy dependent bath.

For DMFT to be useful, need 5 band (“d” orbitals) and 7 band (“f” orbitals) impurity solver -- very **complex atom**

This was hard to solve until recently ... invention of CTQMC (2007).

# Diagrammatic Monte Carlo



Series expansion in  $U$  leads to strong sign problem when Hunds coupling is present.

**Good news: Anderson-Yuval mapping (1970) mapping from expansion in  $U$  to expansion in hybridization**

**Use Continuous time quantum MC on Anderson Yuval problem:**

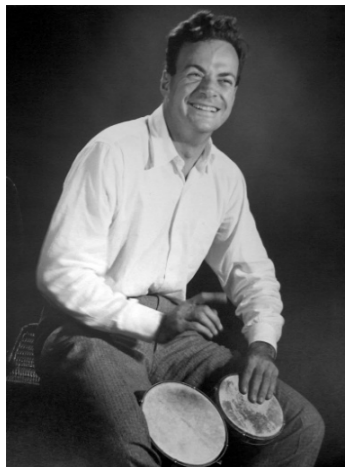
General impurity problem:

$$Z = \int D[\psi^\dagger \psi] e^{-S_{atom} - \int_0^\beta d\tau \int_0^\beta d\tau' \sum_{\alpha\alpha'} \psi_\alpha^\dagger(\tau) \Delta(\tau - \tau') \psi_{\alpha'}(\tau')}$$

Power expansion in terms  $\Delta$ , gives series of Feynman diagrams:

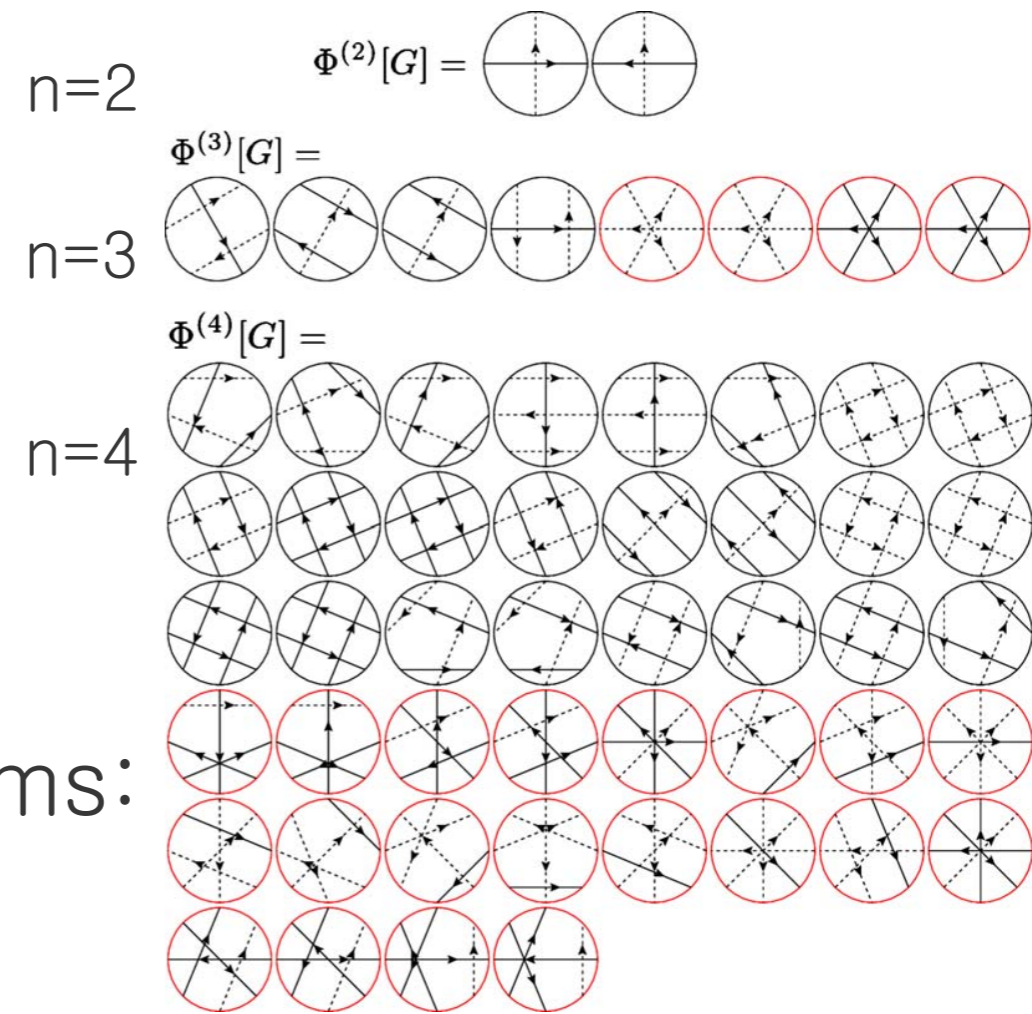
Feynman diagrams

$$Z = Z_{atom} \sum_k \frac{1}{k!} \int_0^\beta d\tau_1 \int_0^\beta d\tau'_1 \cdots \int_0^\beta d\tau_k \int_0^\beta d\tau'_k \sum_{\alpha_1\alpha'_1, \alpha_2\alpha'_2, \dots, \alpha_k\alpha'_k} \langle T_\tau \psi_{\alpha'_1}(\tau'_1) \psi_{\alpha_1}^\dagger(\tau_1) \cdots \psi_{\alpha'_k}(\tau'_k) \psi_{\alpha_k}^\dagger(\tau_k) \rangle_{atom} \times \frac{1}{k!} \text{Det} \begin{pmatrix} \Delta_{\alpha_1\alpha'_1}(\tau_1, \tau'_1) & \Delta_{\alpha_2\alpha'_2}(\tau_2, \tau'_2) & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots \\ \Delta_{\alpha_k\alpha'_k}(\tau_k, \tau'_k) & \cdots & \cdots & \Delta_{\alpha_k\alpha'_k}(\tau_k, \tau'_k) \end{pmatrix}$$





Continuous time quantum MC  
 in hybridization expansion  
**Completely changed the  
 DMFT  
 predictive power**



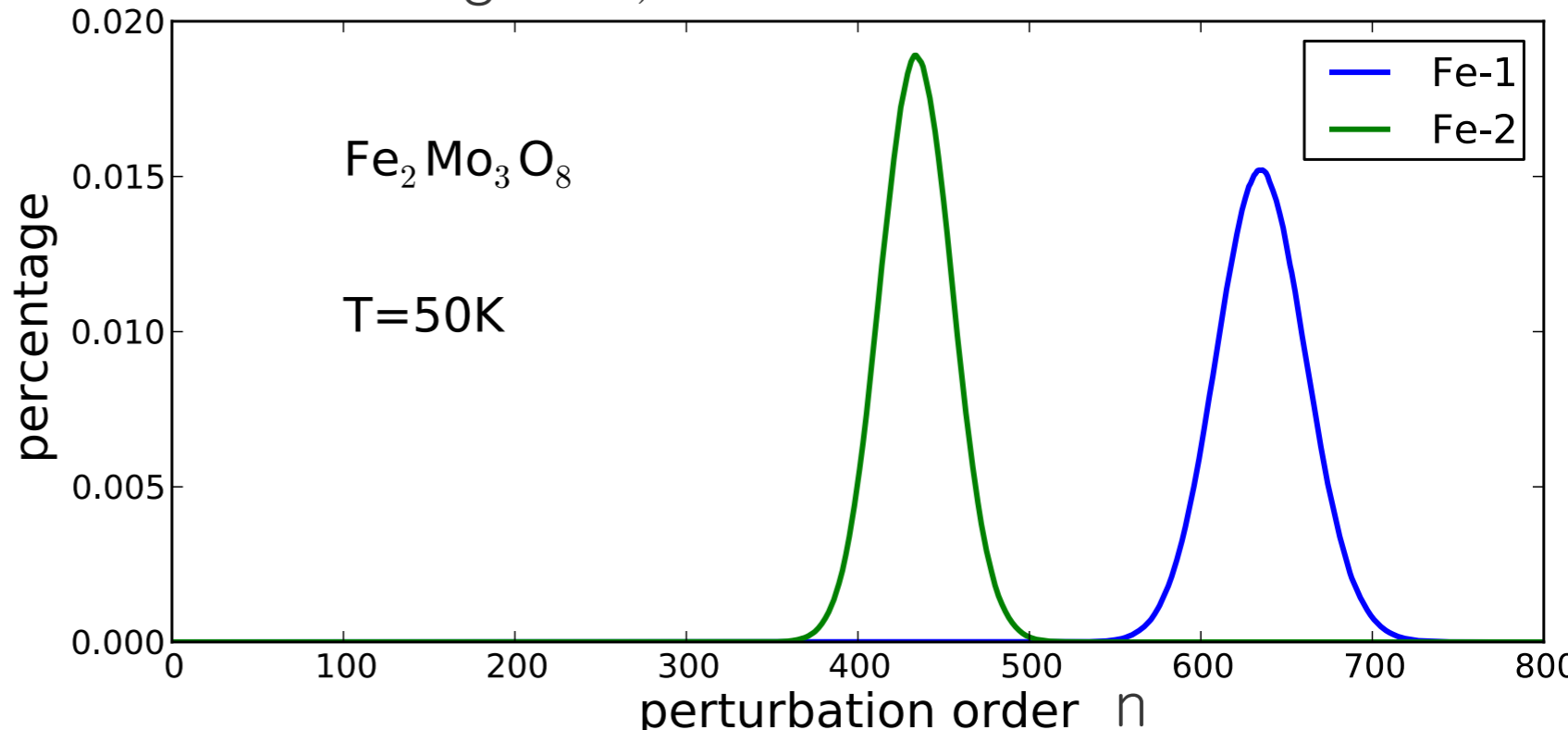
Feynman diagrams:

Metropolis sampling over the diagrams, very efficient because perturbation order is Gaussian in order  $k$  peaked at Kinetic-energy/ $T$ .

random walk in space of diagrams, order 700 reachable

**Virtues:**

- Exact method: samples all diagrams!
- Allows correct treatment of multiplets



# DFT In the LW language

---

We can get DFT by  $\Phi[\{G\}] \rightarrow E_H[\rho] + E_{XC}[\rho]$

The LW functional then leads to identical equations as DFT.

Exact DFT gives exact ground state energy and charge density. But in this approach DFT is an approximation for the Green's function, which gives an approximate spectra, i.e., bands. The spectra can then be interpreted as physical within such approximation for  $\Phi[\{G\}]$

***The fact that bands are very reasonable within LDA/GGA is an indication that correlations are very local in real space.***

*Weaker statement : The picture in which correlations are treated as local is very good — convergence faster when considering local correlations rather than long range correlations.*



# An illustrative example for local correlations

## Variational Diag-MC for electron gas

$$L = L_0 + \Delta L(\xi)$$

Kun Chen & K. Haule, [arXiv:1809.04651](https://arxiv.org/abs/1809.04651)

$$L_0 = \sum_{\mathbf{k}\sigma} \psi_{\mathbf{k}\sigma}^\dagger \left( \frac{\partial}{\partial \tau} - \mu + \frac{\mathbf{k}^2}{2m} \right) \psi_{\mathbf{k}\sigma} + \frac{e^2}{2V} \sum_{\mathbf{q} \neq 0} \phi_{\mathbf{q}}^\dagger \frac{q^2}{8\pi} \phi_{\mathbf{q}}$$

$$\Delta L = \sqrt{\xi} \frac{ie}{2V} \sum_{\mathbf{q} \neq 0} \phi_{\mathbf{q}} \rho(-\mathbf{q}) + \phi_{\mathbf{q}}^\dagger \rho(\mathbf{q})$$

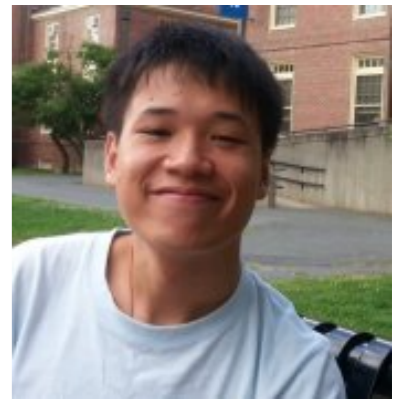
$$\phi_{\mathbf{q}}(\mathbf{r})$$

boson that mediates the interaction

$$\psi_{\mathbf{k}\sigma}(\mathbf{r})$$

electron operator

# Variational Diag-MC for electron gas



Kun Chen

$$L = L_0 + \Delta L(\xi)$$

$$L_0 = \sum_{\mathbf{k}\sigma} \psi_{\mathbf{k}\sigma}^\dagger \left( \frac{\partial}{\partial \tau} - \mu + \frac{\mathbf{k}^2}{2m} + v_{\mathbf{k}}(\xi = 1) \right) \psi_{\mathbf{k}\sigma} + \frac{e^2}{2V} \sum_{\mathbf{q} \neq 0} \phi_{\mathbf{q}}^\dagger \frac{q^2 + \lambda_{\mathbf{q}}}{8\pi} \phi_{\mathbf{q}}$$

$$\Delta L = - \sum_{\mathbf{k}\sigma} \psi_{\mathbf{k}\sigma}^\dagger v_{\mathbf{k}}(\xi) \psi_{\mathbf{k}\sigma} - \xi \frac{e^2}{2V} \sum_{\mathbf{q} \neq 0} \phi_{\mathbf{q}}^\dagger \frac{\lambda_{\mathbf{q}}}{8\pi} \phi_{\mathbf{q}} + \sqrt{\xi} \frac{ie}{2V} \sum_{\mathbf{q} \neq 0} \phi_{\mathbf{q}} \rho(-\mathbf{q}) + \phi_{\mathbf{q}}^\dagger \rho(\mathbf{q})$$

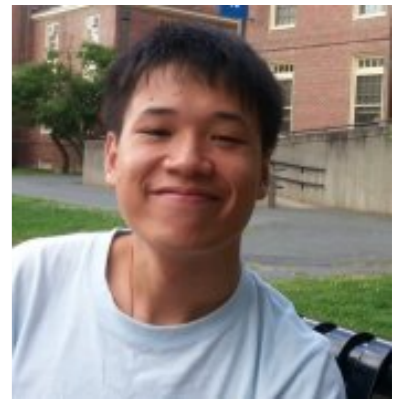
$$\phi_{\mathbf{q}}(\mathbf{r})$$

boson that mediates the interaction

$$\psi_{\mathbf{k}\sigma}(\mathbf{r})$$

electron operator

# Variational Diag-MC for electron gas

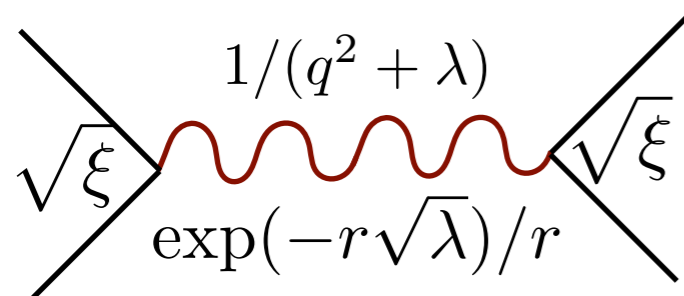


Kun Chen

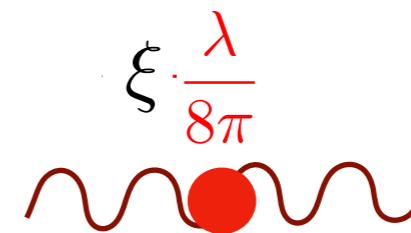
$$L = L_0 + \Delta L(\xi)$$

$$L_0 = \sum_{\mathbf{k}\sigma} \psi_{\mathbf{k}\sigma}^\dagger \left( \frac{\partial}{\partial \tau} - \mu + \frac{\mathbf{k}^2}{2m} + v_{\mathbf{k}}(\xi = 1) \right) \psi_{\mathbf{k}\sigma} + \frac{e^2}{2V} \sum_{\mathbf{q} \neq 0} \phi_{\mathbf{q}}^\dagger \frac{q^2 + \lambda_{\mathbf{q}}}{8\pi} \phi_{\mathbf{q}}$$

$$\Delta L = - \sum_{\mathbf{k}\sigma} \psi_{\mathbf{k}\sigma}^\dagger v_{\mathbf{k}}(\xi) \psi_{\mathbf{k}\sigma} - \xi \frac{e^2}{2V} \sum_{\mathbf{q} \neq 0} \phi_{\mathbf{q}}^\dagger \frac{\lambda_{\mathbf{q}}}{8\pi} \phi_{\mathbf{q}} + \sqrt{\xi} \frac{ie}{2V} \sum_{\mathbf{q} \neq 0} \phi_{\mathbf{q}} \rho(-\mathbf{q}) + \phi_{\mathbf{q}}^\dagger \rho(\mathbf{q})$$



Coulomb is static and short ranged.

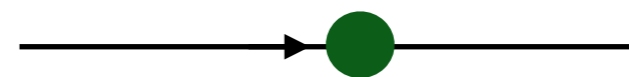


Counter terms make sure that we arrive at the exact answer at large p.o. for any  $\lambda$

$$G_{\mathbf{k}}^0(i\omega) = \frac{1}{i\omega + \mu - \frac{k^2}{2m} - v_{\mathbf{k}}}$$

electron propagator is optimized at each order (preserve Luttinger's theorem)

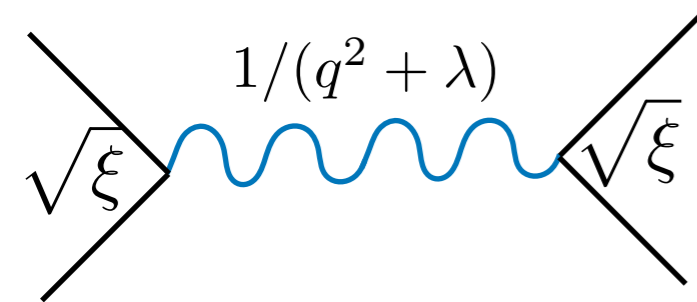
$$v_{\mathbf{k}}(\xi) = \xi(\Sigma_{\mathbf{k}}^x - \Sigma_{k_F}^x) + \xi^2 s_2 + \xi^3 s_3 + \dots$$



counter-term to converge to the exact result

# An illustrative example for local correlations

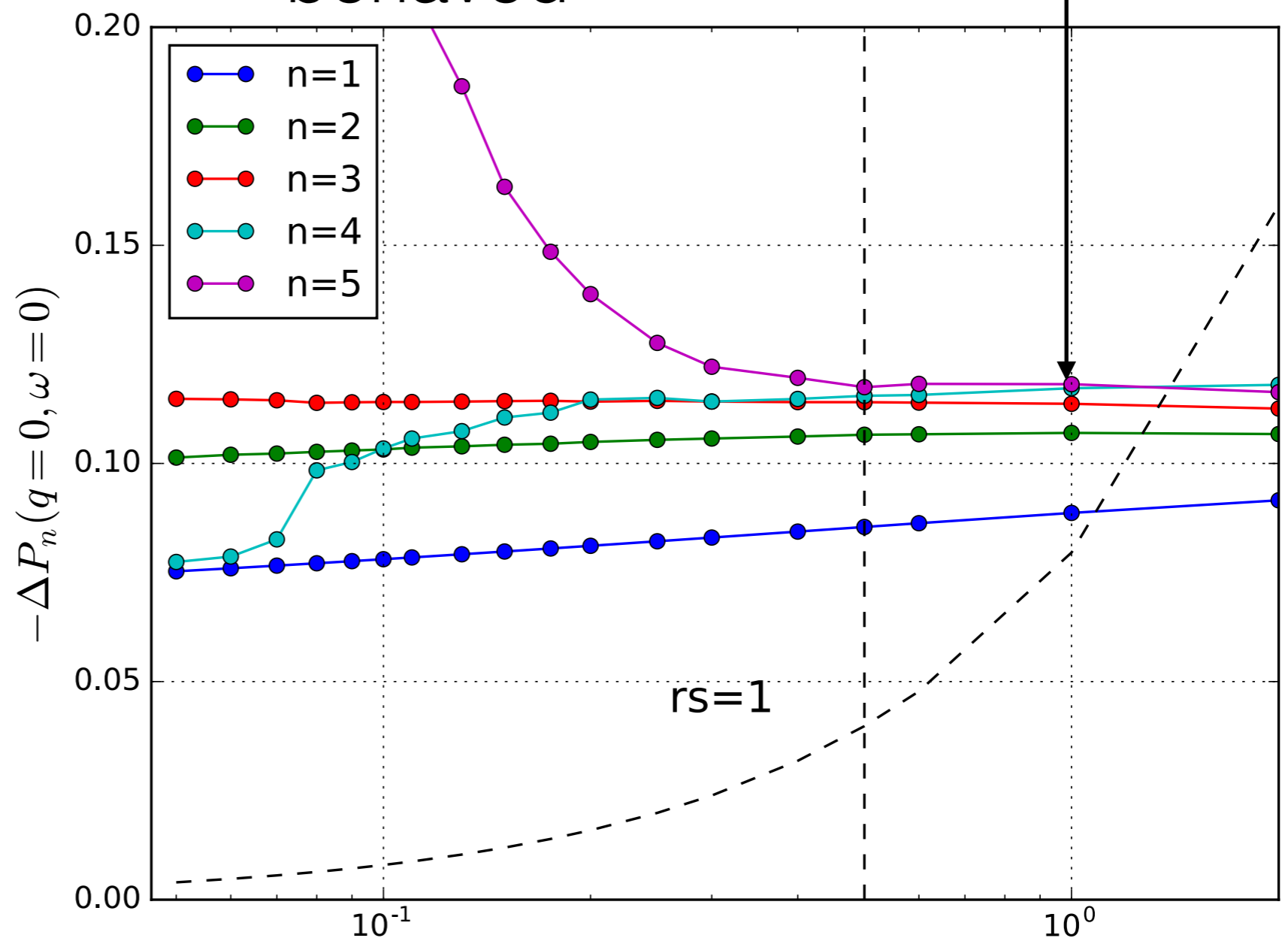
When expanding with respect to screened interaction, the convergence is well behaved, and rapid. Locality of correlations in solids helps rapid convergence.



$$V(r) = \frac{e^{-r\sqrt{\lambda}}}{r}$$

any type of  
perturbation ill-  
behaved

essentially  
exact solution



# Spin-susceptibility of electron gas

Calculated values at different densities.

VDMC get four significant digits at order  $N=6$ .

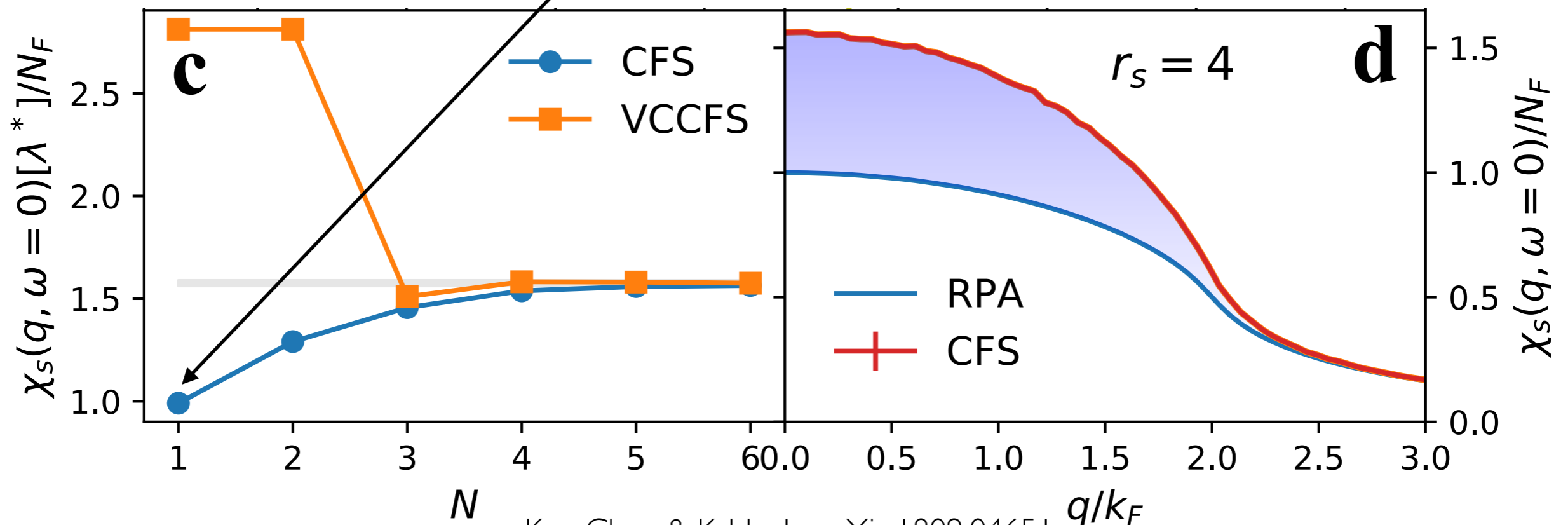
Consistent with literature, but significantly more precise.

$$\frac{1}{n} = \frac{4\pi r_s^3}{3}$$

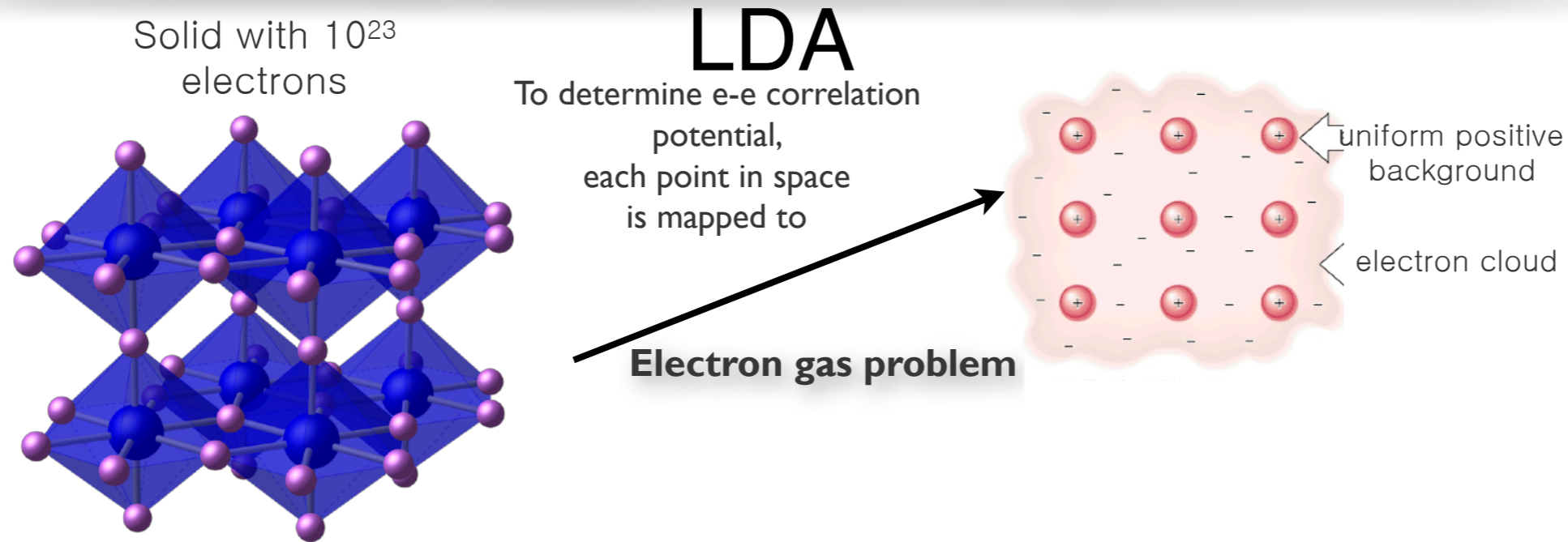
$r_s$	$\chi_s/N_F$	literature
1	1.152(2)	1.15-1.16
2	1.296(6)	1.27-1.31
3	1.438(9)	1.39-1.46
4	1.576(9)	1.51-1.62

Note:  $G_0W_0$  is the first order

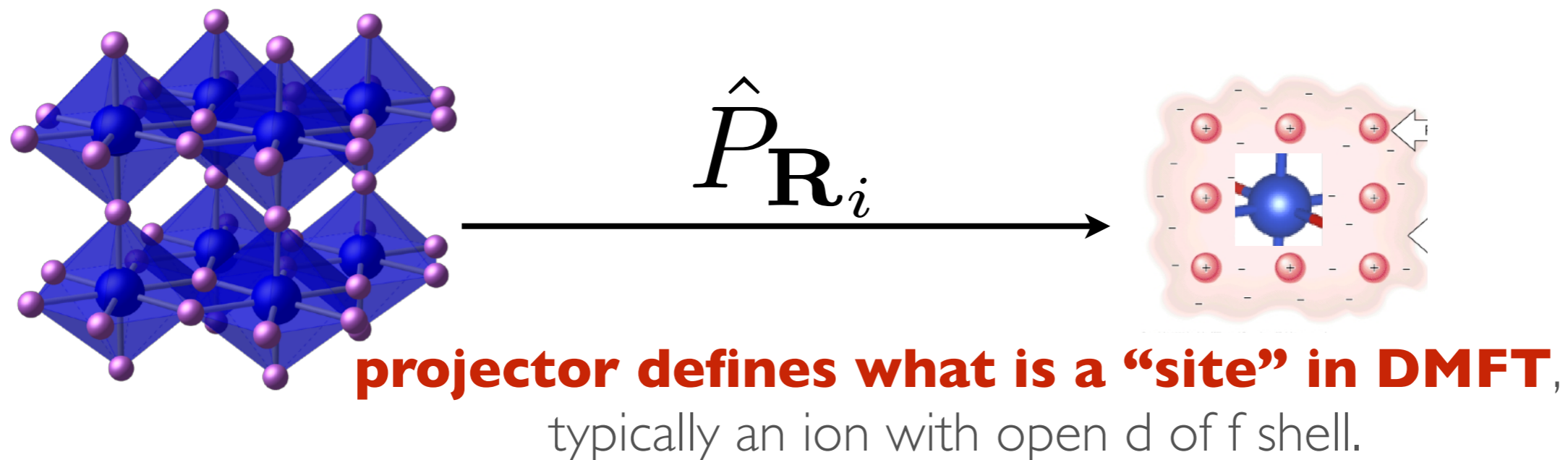
spin susceptibility for different momenta.  
RPA 57% underestimates.



# Back to DMFT: How is correlation potential determined?



In DMFT we want to lift the restriction and compute all correlations local to a given site (not given point in space).



# The continuous DMFT problem

DMFT approximation:  $\Phi[\{G\}] \rightarrow \sum_{\mathbf{R}_i} \Phi[\{\hat{P}_{\mathbf{R}_i} G\}]$

in continuum requires **discretization** of projector,

$$\hat{P}_{\mathbf{R}_i} \rightarrow P_{\mathbf{R}_i}(\alpha\beta) = \int d\mathbf{r}d\mathbf{r}' \mathcal{P}_{\mathbf{R}_i}(\alpha\beta; \mathbf{r}\mathbf{r}')$$

complete set of orbitals  
centered on a site:

$$P_{\mathbf{R}_i}(\alpha\beta) = \int d\mathbf{r}d\mathbf{r}' \phi_\alpha(\mathbf{r} - \mathbf{R}_i) \phi_\beta^*(\mathbf{r}' - \mathbf{R}_i)$$

where  $\phi_\alpha(\mathbf{r} - \mathbf{R}_i) \equiv \langle \mathbf{r} | \phi_\alpha^i \rangle$  forms a basis on a given atom

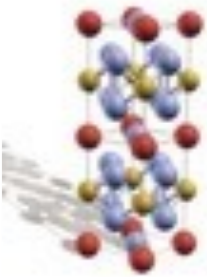
so that:

$$G_{local}^i(\mathbf{r}, \mathbf{r}') = \sum_{\alpha\beta} \langle \mathbf{r} | \phi_\alpha^i \rangle \langle \phi_\alpha^i | G | \phi_\beta^i \rangle \langle \phi_\beta^i | \mathbf{r}' \rangle$$

↑  
quasi atomic orbitals  
(locally complete set)

$\alpha, \beta$  are orbital-spin indices

# DFT+Embedded Dynamical Mean Field Theory Functional



$$\Gamma[G] = Tr \log G - Tr((G_0^{-1} - G^{-1})G) + E_{Vc}^{H+XC}[\rho] + \Phi_{V_{DMFT}}^{DMFT}[G_{local}] - \Phi_{V_{DMFT}}^{H+XC}[\rho_{local}]$$

Green's function  $\uparrow$   
 $G_0^{-1} = [i\omega_n + \mu + \nabla^2 - V_{nuc}(\mathbf{r})]\delta(\mathbf{r} - \mathbf{r}')$   
 non-interacting part of G  $\uparrow$

Hartree + XC functional  $\uparrow$   
 sum of all "local" Feynman diagrams for correlated ions.  $\uparrow$   
 double-counted interaction (we know exactly)  $\uparrow$

$\Gamma[G]$  is stationary and gives free energy of the system.

$$\frac{\delta\Gamma[G]}{\delta G} = 0 \quad \text{because} \quad G^{-1} - G_0^{-1} + V_{H+XC}\delta(\mathbf{r} - \mathbf{r}')\delta(\tau - \tau') +$$

$$+ \hat{P} \frac{\delta\Phi^{DMFT}[G_{local}]}{\delta G_{local}} - \hat{P} \frac{\delta\Phi^{DC}[\rho_{local}]}{\delta \rho_{local}} \delta(\mathbf{r} - \mathbf{r}')\delta(\tau - \tau') = 0$$



# Embedded Dynamical Mean Field Theory Functional

Details on extremization:

$$\frac{\delta}{\delta G} \Gamma[\{G\}] = \frac{\delta}{\delta G} (\text{Tr} \log G - \text{Tr}((G_0^{-1} - G^{-1})G)) + \frac{\delta E_{V_c}^{H+XC}[\rho]}{\delta G} + \frac{\delta \sum_{\mathbf{R}_i} \Phi_{V_{DMFT}}[\{\int d\mathbf{r}d\mathbf{r}' \phi_\alpha(\mathbf{r} - \mathbf{R}_i)G(\mathbf{r}\mathbf{r}')\phi_\beta^*(\mathbf{r}' - \mathbf{R}_i)\}]}{\delta G} - \frac{\delta \sum_{\mathbf{R}_i} \Phi_{V_{DMFT}}^{H+XC}[\{\int d\mathbf{r}d\mathbf{r}' \phi_\alpha(\mathbf{r} - \mathbf{R}_i)\rho(\mathbf{r}\mathbf{r}')\phi_\beta^*(\mathbf{r}' - \mathbf{R}_i)\}]}{\delta G}$$

or

$$\begin{aligned} \frac{\delta}{\delta G} \Gamma[\{G\}] = & G^{-1} - G_0^{-1} + \frac{\delta E_{V_c}^{H+XC}[\rho]}{\delta \rho} \delta(\mathbf{r} - \mathbf{r}')\delta(\tau - \tau') \quad \left(\rho(\mathbf{r}) = \delta(\mathbf{r} - \mathbf{r}')\delta(\tau - \tau')G(\mathbf{r}\tau, \mathbf{r}'\tau')\right) \\ & + \sum_{\alpha\beta} \frac{\delta \Phi_{V_{DMFT}}[\{G_{local}^i\}]}{\delta G_{local\beta\alpha}^i} \phi_\alpha(\mathbf{r} - \mathbf{R}_i)\phi_\beta^*(\mathbf{r}' - \mathbf{R}_i) \\ & - \sum_{\alpha\beta} \frac{\delta \Phi_{V_{DMFT}}^{H+XC}[\{\rho_{local}\}]}{\delta \rho_{local\beta\alpha}} \phi_\alpha(\mathbf{r} - \mathbf{R}_i)\delta(\tau - \tau')\phi_\beta^*(\mathbf{r}' - \mathbf{R}_i) \} = 0 \end{aligned}$$

finally

$$G^{-1} = G_0^{-1} - V_{H+XC}(\mathbf{r})\delta(\mathbf{r} - \mathbf{r}')\delta(\tau - \tau') - \langle \mathbf{r} | \phi_\alpha^i \rangle (\Sigma^{imp} - V^{DC})_{\alpha\beta} \langle \phi_\beta^i | \mathbf{r}' \rangle$$

where

$$\Sigma_{\alpha\beta}^{imp} = \frac{\delta \Phi_{V_{DMFT}}[\{G_{local}^i\}]}{\delta G_{local\beta\alpha}^i} \quad \text{and} \quad V_{\alpha\beta}^{DC} = \frac{\delta \Phi_{V_{DMFT}}^{H+XC}[\{\rho_{local}\}]}{\delta \rho_{local\beta\alpha}} \delta(\tau - \tau')$$

# Embedded Dynamical Mean Field Theory Functional

$$G^{-1} = G_0^{-1} - \underbrace{V_{H+XC}(\mathbf{r})\delta(\mathbf{r} - \mathbf{r}')\delta(\tau - \tau')}_{DFT} - \underbrace{\langle \mathbf{r} | \phi_\alpha^i \rangle (\Sigma^{imp} - V^{DC})_{\alpha\beta} \langle \phi_\beta^i | \mathbf{r}' \rangle}_{\text{quantum impurity } S. \text{ embedded}}$$

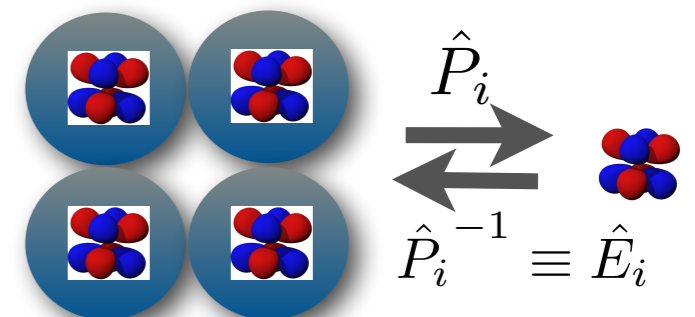
where  $\Sigma_{\alpha\beta}^{imp} = \frac{\delta\Phi_{VDMFT}[\{G_{local}^i\}]}{\delta G_{local\beta\alpha}^i}$  and  $V_{\alpha\beta}^{DC} = \frac{\delta\Phi_{VDMFT}^{H+XC}[\{\rho_{local}\}]}{\delta\rho_{local\beta\alpha}}\delta(\tau - \tau')$

On each correlated site  $\mathbf{R}_i$  we have to solve a quantum impurity model with  $\alpha\beta$  orbitals  $\Sigma_{\alpha\beta}^{imp} = \frac{\delta\Phi_{VDMFT}[\{G_{local}^i\}]}{\delta G_{local\beta\alpha}^i}$

And **Embed** self-energies to continuum space by

$$\langle \mathbf{r} | \phi_\alpha^i \rangle \Sigma_{\alpha\beta}^{imp} \langle \phi_\beta^i | \mathbf{r}' \rangle$$

Notice that once the projector is defined, embedding is uniquely given by the same matrix elements of  $\mathcal{P}_{\mathbf{R}_i}(\alpha\beta; \mathbf{r}\mathbf{r}') = \phi_\alpha(\mathbf{r} - \mathbf{R}_i)\phi_\beta^*(\mathbf{r}' - \mathbf{R}_i)$



# The continuous DMFT problem

---

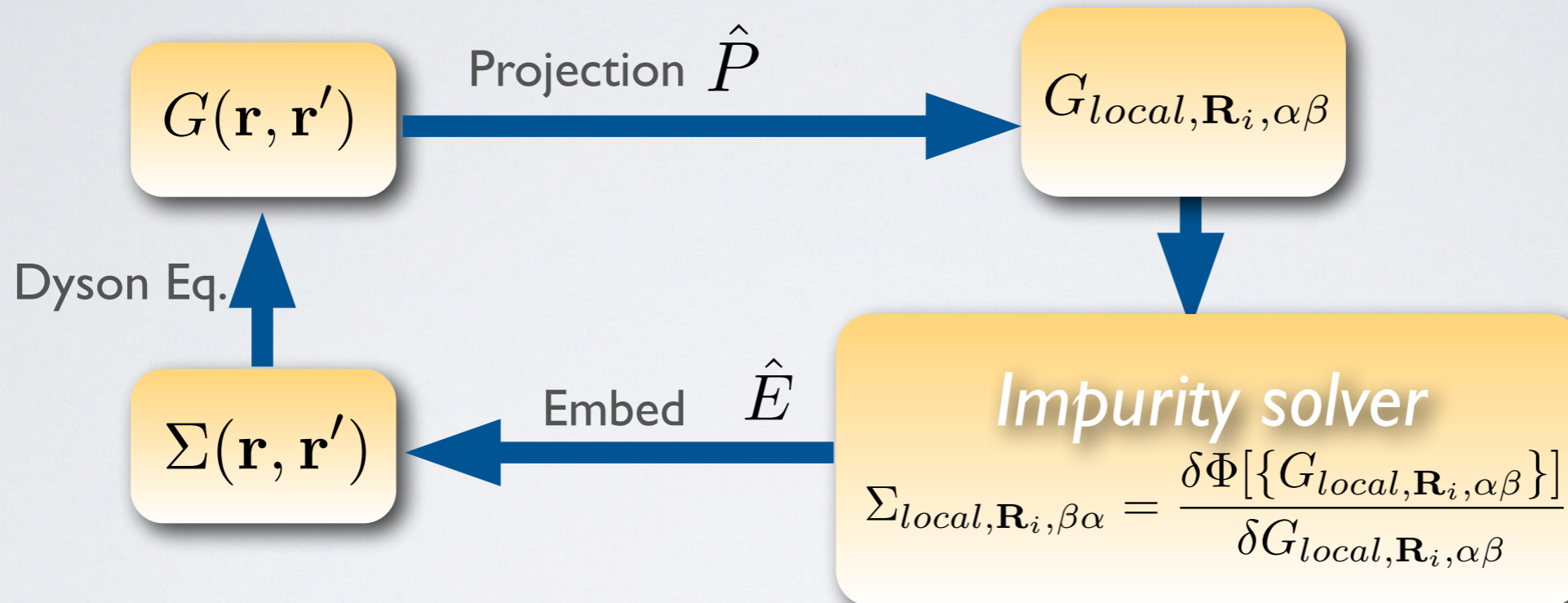
DFT+DMFT methods in literature *differ* in definition of the projector

*Strengths:* DMFT is flexible and allows one to optimize projector (easier to work with low energy Wannier functions, but more localized projectors are more universal and work well in any system, f-systems or molecules).

*Weaknesses :* DFT+DMFT literature is confusing. Results are different when using low-energy Wannier functions or more localized quasi-atomic orbitals (at least  $U$  is different), but reader is rarely warned.

# SUMMARY: PROJECT/EMBED

Phys. Rev. B 81, 195107 (2010), K. Haule, Chuck-Hou Yee, Kyoo Kim.



DMFT in continuum problem (Project/Embed):

Projection: 
$$G_{local, \mathbf{R}_i, \alpha\beta} = \int d\mathbf{r} d\mathbf{r}' \Phi_\alpha(\mathbf{r} - \mathbf{R}_i) G(\mathbf{r}, \mathbf{r}') \Phi_\beta^*(\mathbf{r}' - \mathbf{R}_i)$$

Embedding: 
$$\Sigma(\mathbf{r}, \mathbf{r}') = \sum_{\mathbf{R}_i, \alpha\beta} \Phi_\alpha^*(\mathbf{r} - \mathbf{R}_i) \Sigma_{local, \mathbf{R}_i, \alpha\beta} \Phi_\beta(\mathbf{r}' - \mathbf{R}_i)$$

Dyson Eq solved in large Hilbert space: 
$$G(\mathbf{r}, \mathbf{r}') = (\delta(\mathbf{r} - \mathbf{r}') (i\omega + \mu + \nabla^2 - V_{ext}(\mathbf{r}) - V_{xc}(\mathbf{r})) - \Sigma^{DMFT}(\mathbf{r}, \mathbf{r}'))^{-1}$$

Requirements: 
$$\frac{\delta P}{\delta G} = 0 \quad \text{and} \quad \text{projector must be separable}$$

# PART 1 EDMFT

---

- What is eDMFT and its connection to DFT.
- Projectors and locality of correlations

**Rev. Mod. Phys. 78, 865 (2006)**

G. Kotliar, S.Y. Savrasov, K. Haule, V. S. Oudovenko, O. Parcollet, and C.A. Marianetti.

**Phys. Rev. B 81, 195107 (2010)**, K. Haule, Chuck-Hou Yee, Kyoo Kim.

## PART 2: STRUCTURAL PREDICTIONS

---

- *Exact double-counting of DFT+eDMFT (PRL 115, 196403 (2015)).*
- *Stationary free energy functional (within Embedded DMFT approach) for structural optimization, PRL 115, 256402 (2015).*
- Implementation of Forces within E-DMFT functional for optimization of internal structural parameter, (**Phys. Rev. B 49, 195146 (2016)**, K. Haule, G.L. Pascut)

# STRUCTURAL PREDICTIONS FOR CORRELATED ELECTRON MATERIALS WITHIN EDMFT

*Kristjan Haule*

<http://hauleweb.rutgers.edu/tutorials/>

Home What is? Install Overview CTQMC MnO FeSe

## DFT + Embedded DMFT Functional\*

Developed by Kristjan Haule at Rutgers University, ©Copyright 2007-2017.



Support:



ACS  
Chemistry for Life™



Blavatnik Awards  
Young Scientists

# PART 1 EDMFTF

---

- What is eDMFT and its connection to DFT.
- Projectors and locality of correlations

**Rev. Mod. Phys. 78, 865 (2006)**

G. Kotliar, S.Y. Savrasov, K. Haule, V. S. Oudovenko, O. Parcollet, and C.A. Marianetti.

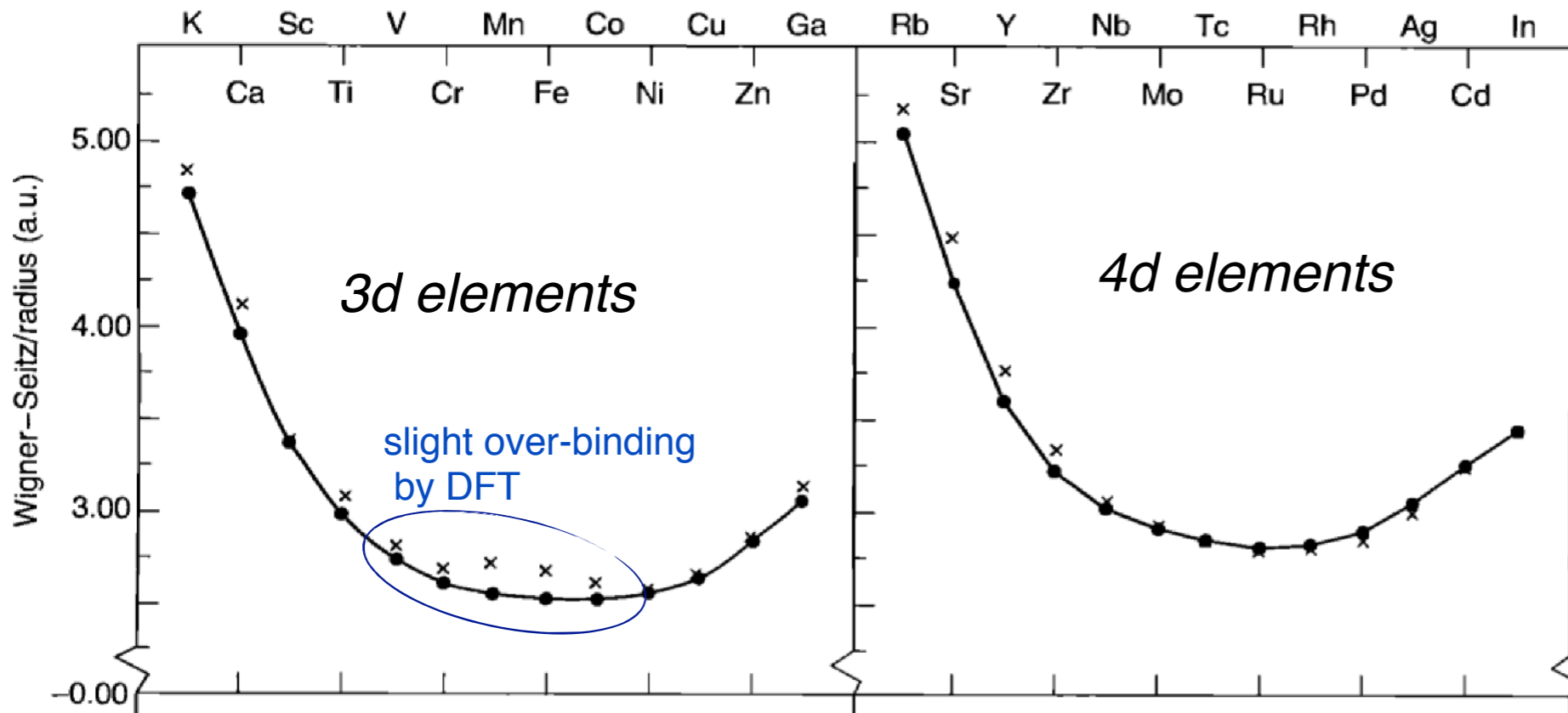
**Phys. Rev. B 81, 195107 (2010)**, K. Haule, Chuck-Hou Yee, Kyoo Kim.

# PART 2 : STRUCTURAL PREDICTIONS

---

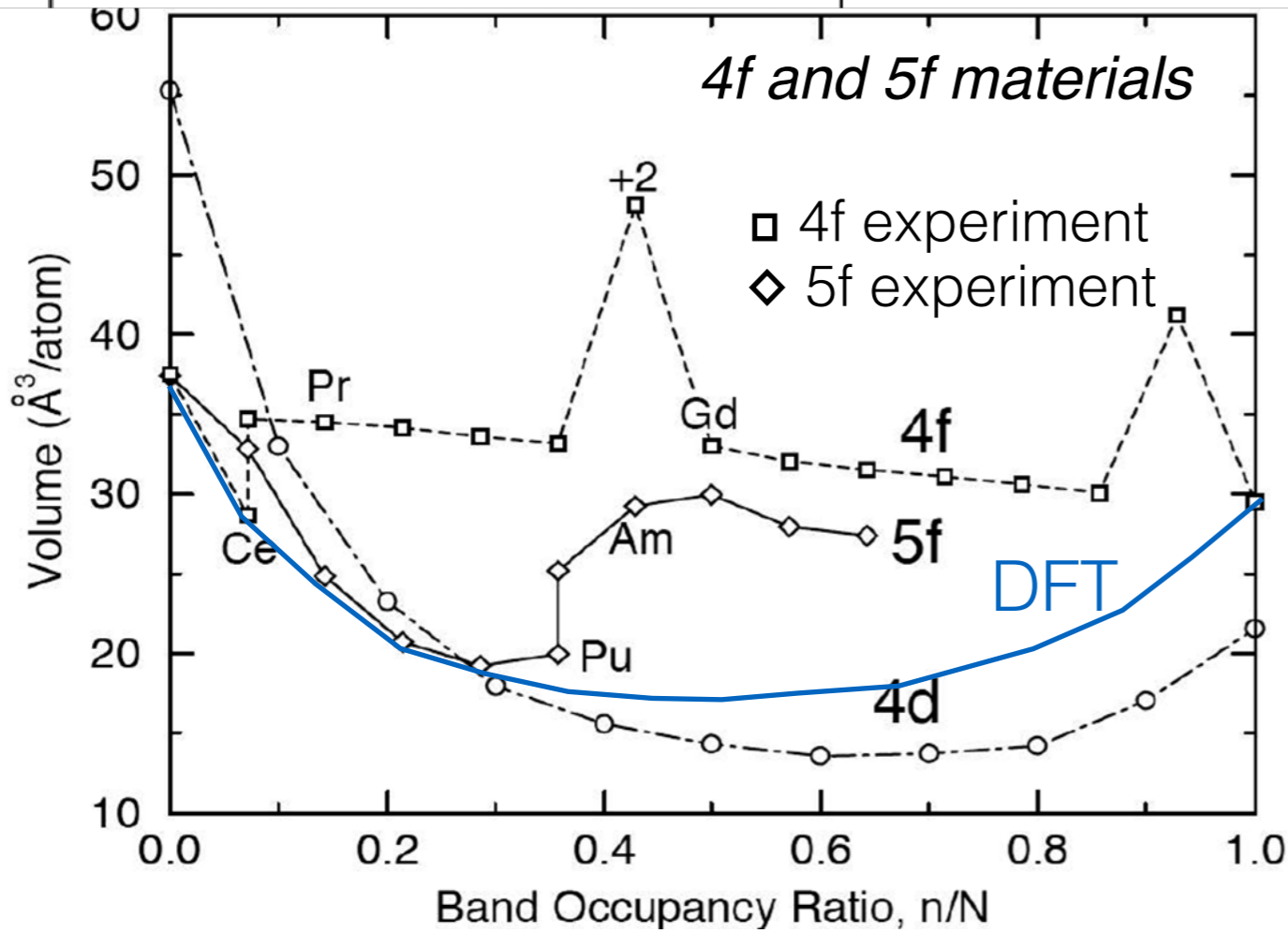
- Structural optimization and *stationary of the free energy functional (within Embedded DMFT approach) for structural optimization, PRL 115, 256402 (2015)*.
- *Exact double-counting of DFT+EDMFTF (PRL 115, 196403 (2015))*.
- Implementation of Forces within E-DMFT functional for optimization of internal structural parameter, (**Phys. Rev. B 49, 195146 (2016)**, K. Haule, G.L. Pascut)

# STRUCTURAL PREDICTIONS: SIZE OF THE IONS / UNIT CELL



*crosses: experiment*  
*black lines: DFT*

DFT predicts very accurately the size of unit cells in 3d&4d elements.



4f elements are essentially localized - no binding versus filling.  
essentially atomic physics.

early 5f elements are quite itinerant, beyond Pu very localized=> DFT fails.

**Conclusion: LDA/GGA pretty good in elemental solids, except in 4f,5f.**

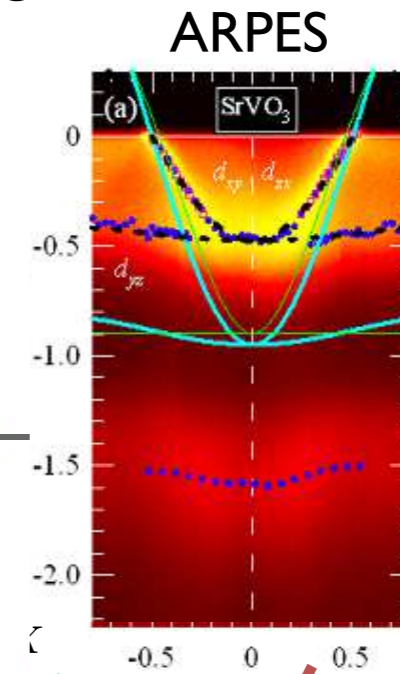
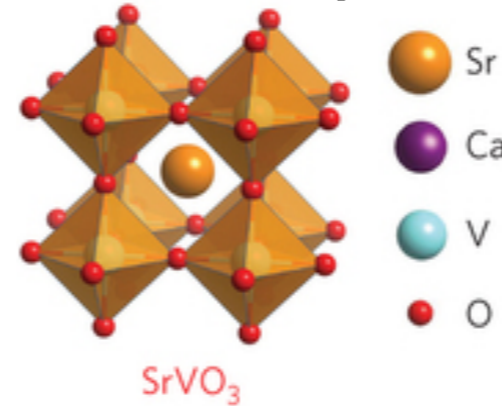


# Lattice constant in DFT

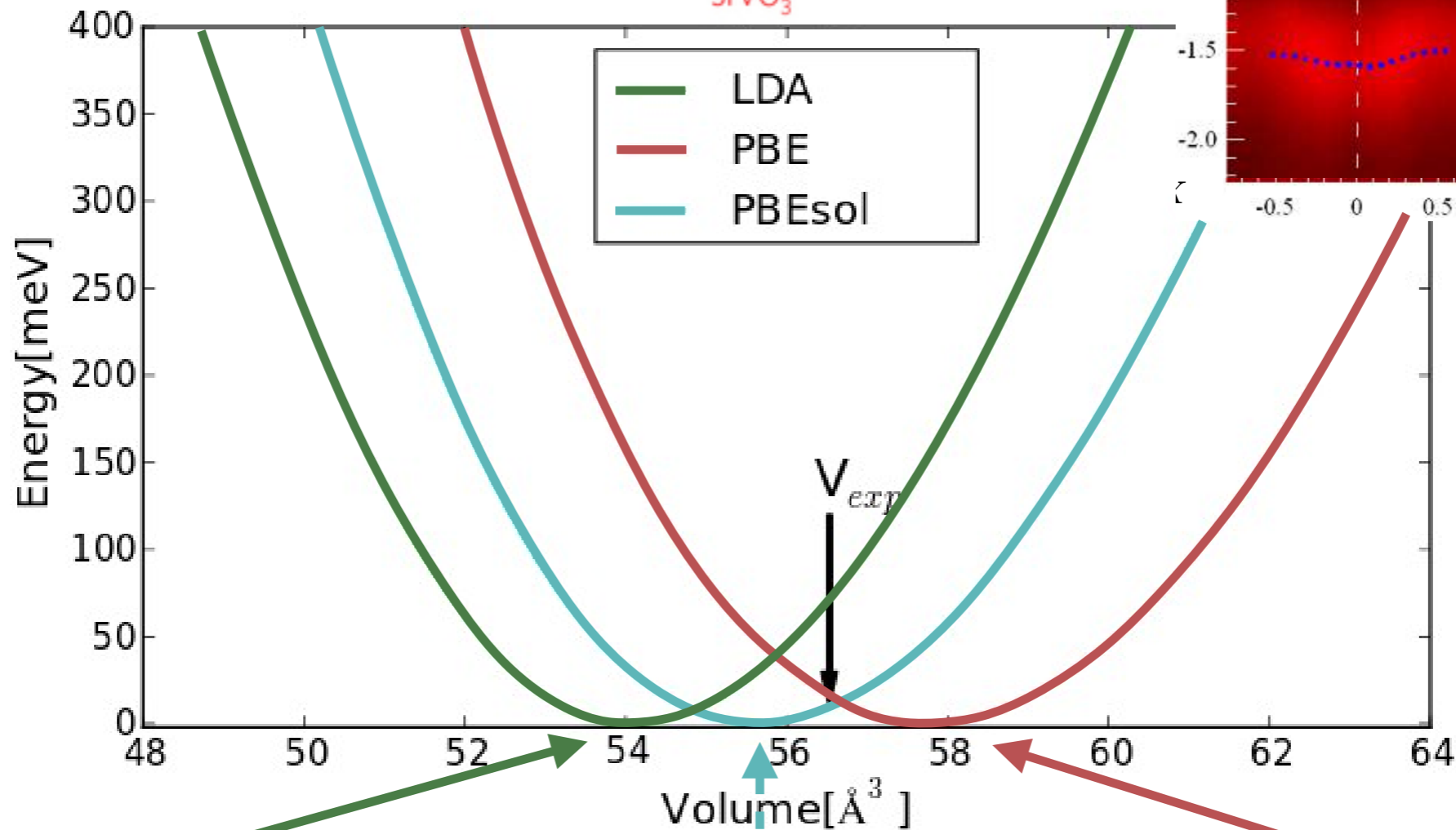
PRL **115**, 256402 (2015), K.H and T. Birol.



## SrVO<sub>3</sub> cubic perovskite:



green : GGA  
blue dots  
and color: exp.



LDA  
underestimates

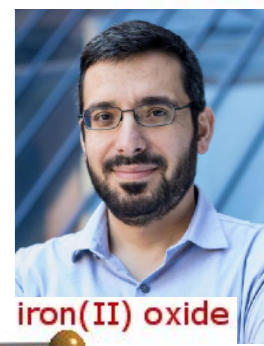
PBEsol  
optimized for lattice constants

PBE  
overestimates

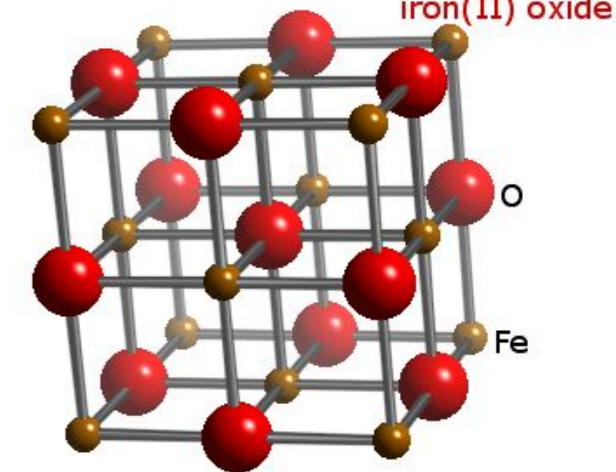
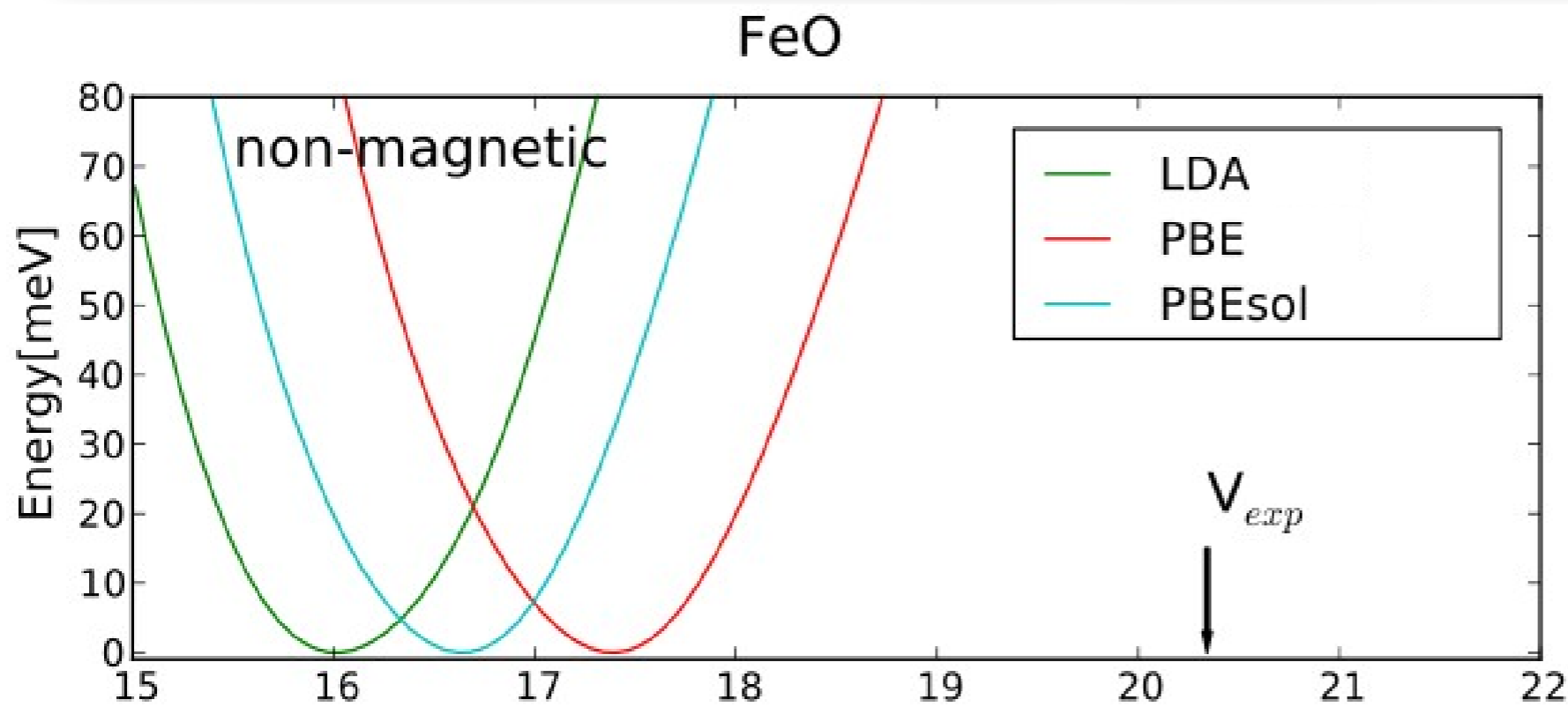
Different DFT functionals: can improve volume, but almost no change to spectra.

# DFT for Mott insulating FeO

PRL **115**, 256402 (2015), K.H and T. Birol.



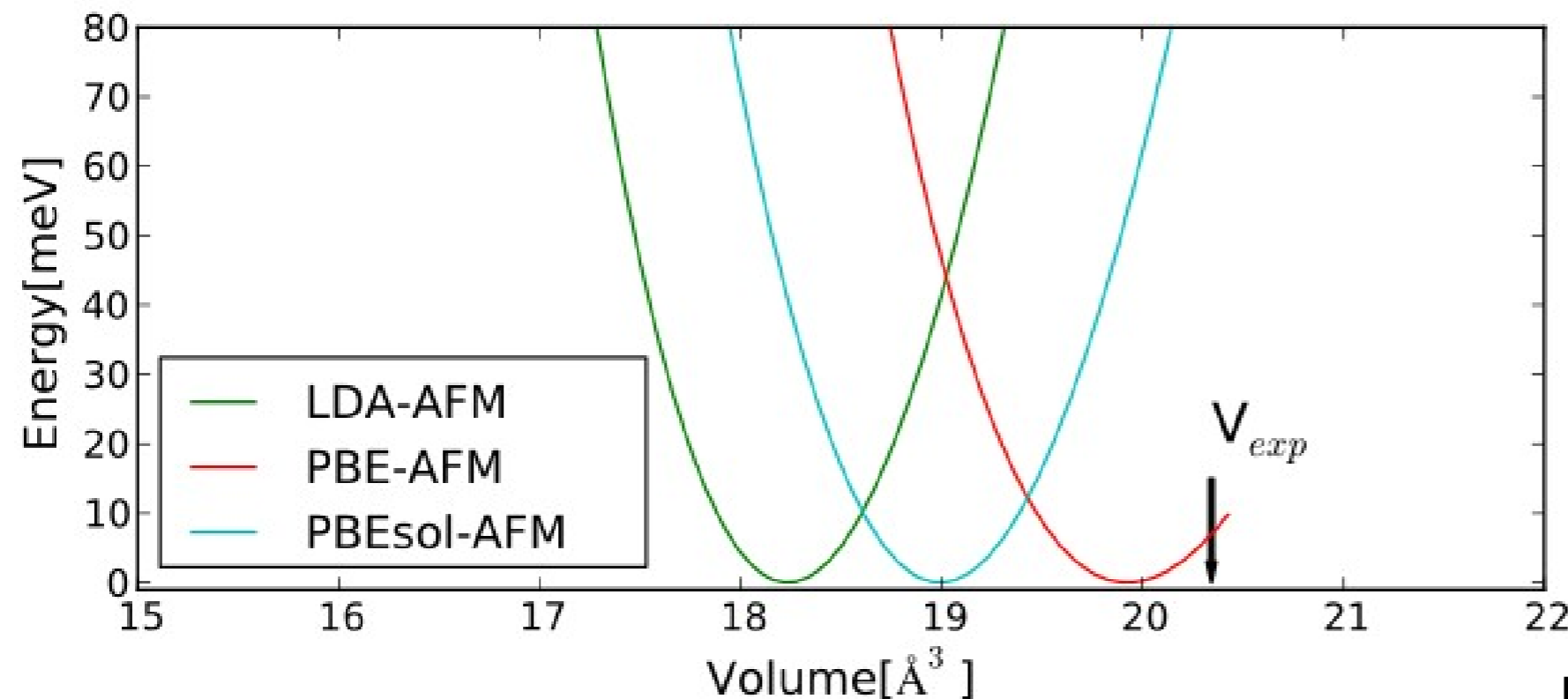
iron(II) oxide



NaCl structure

Missing local  
fluctuating moments

Overbinding problem



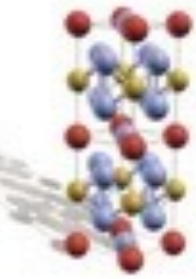
Ordered moments  
improve, not good  
enough.

Even PBE  
underestimates volume.

PRL **115**, 256402 (2015), K.H and T. Birol.

# Question

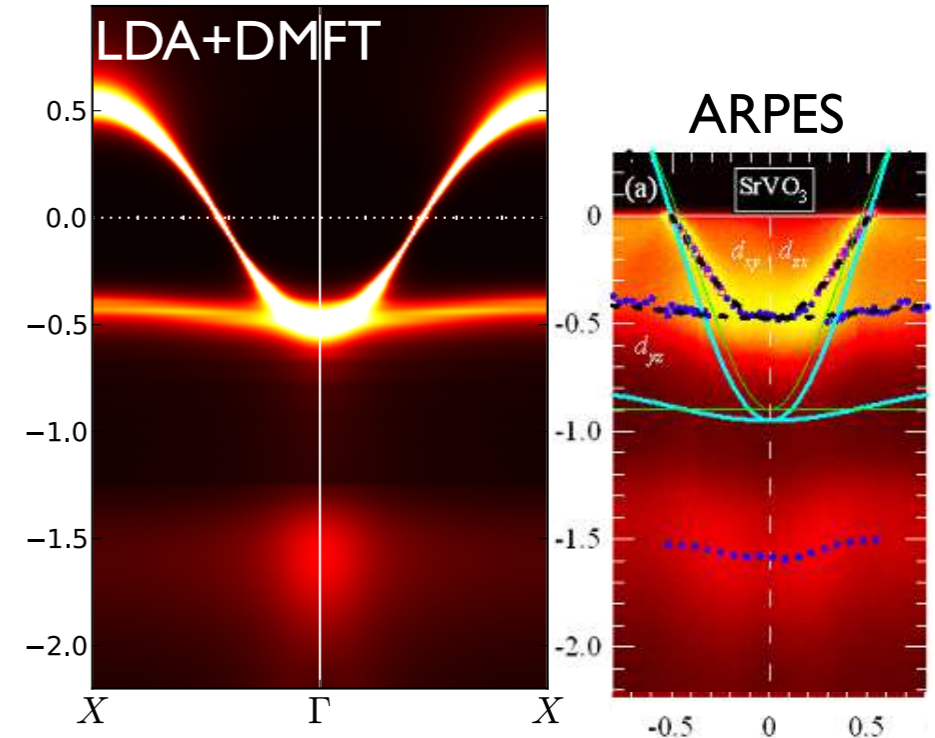
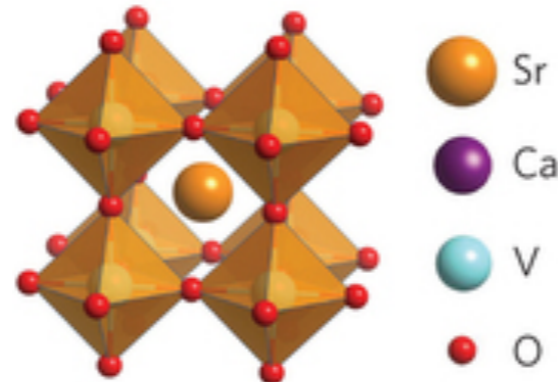
---



Can we consistently improve energies and spectra of correlated solids?

# STRUCTURES OF A CORRELATED SOLID, LIKE OXIDES

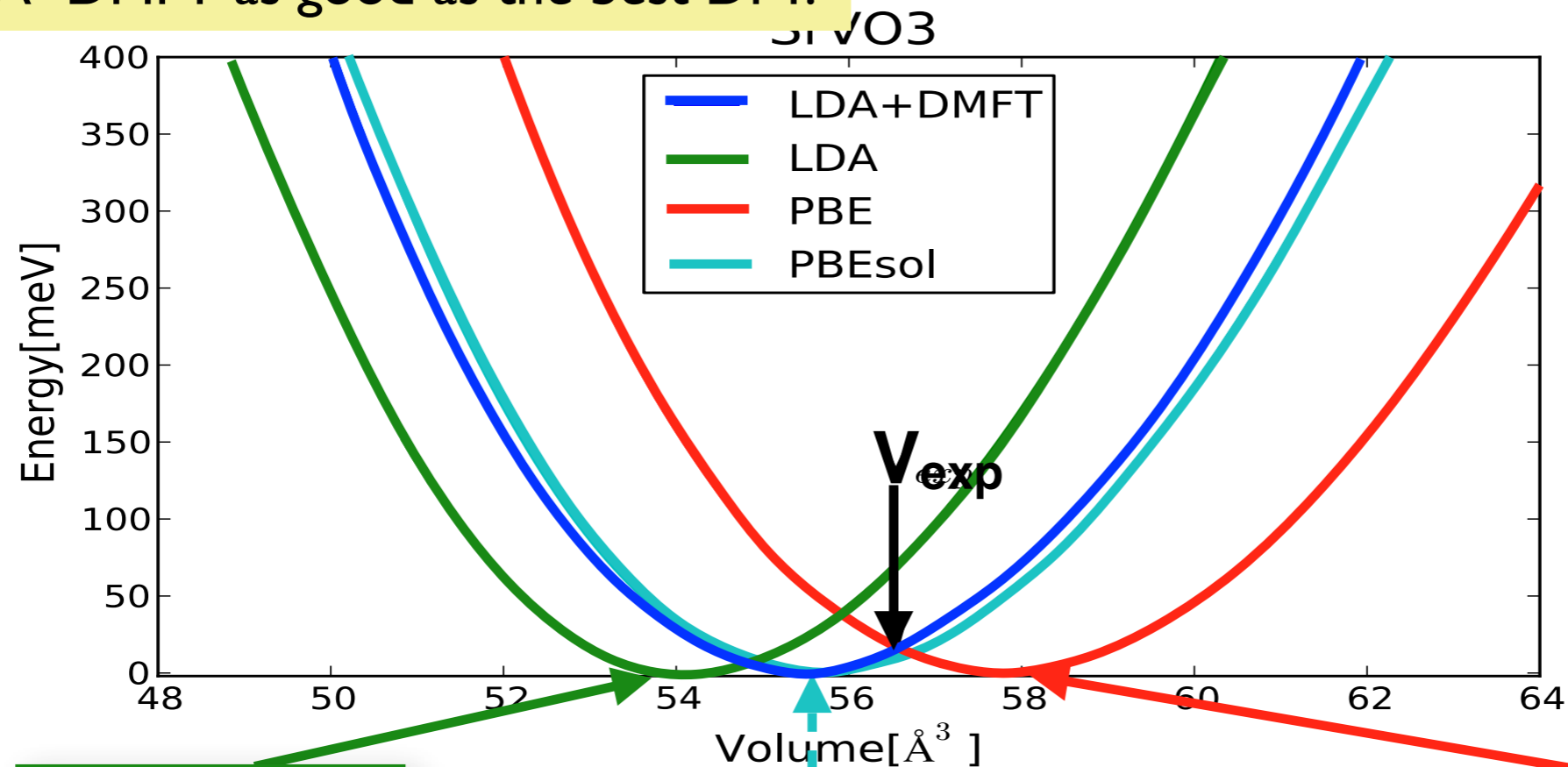
## SrVO<sub>3</sub> cubic perovskite:



DTF-DMFT: Haule & Birol, PRL 115, 256402 (2015).

DMFT: correlated metal with  $m^*/m \sim 3$ .

EOS of LDA+DMFT as good as the best DFT.

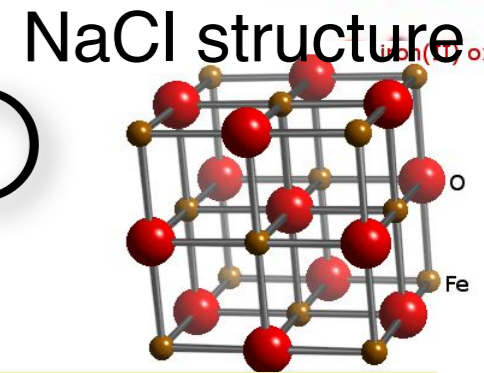


LDA underestimates

DMFT and PBEsol very similar

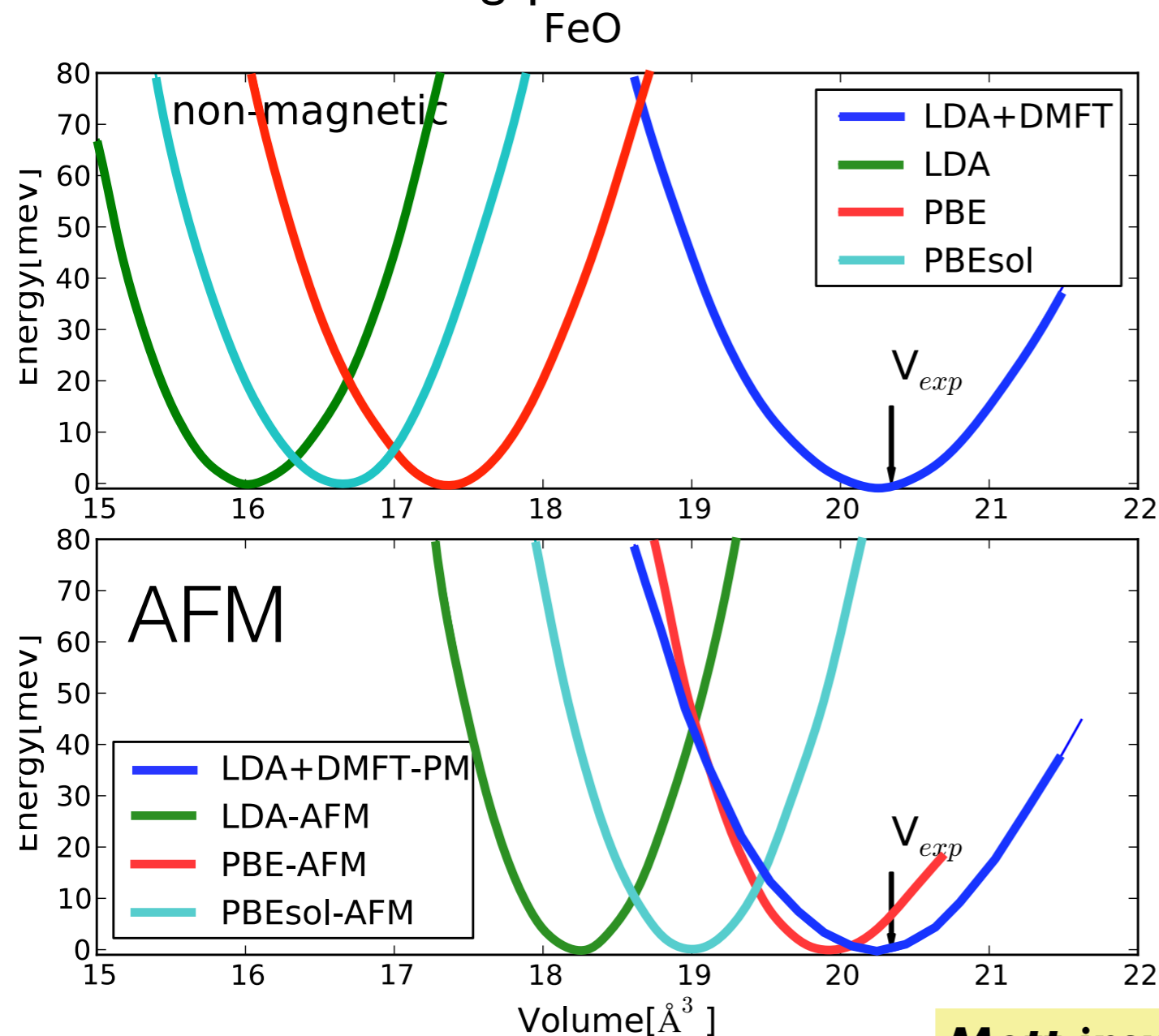
PBE overestimates

# paramagnetic Mott insulator FeO

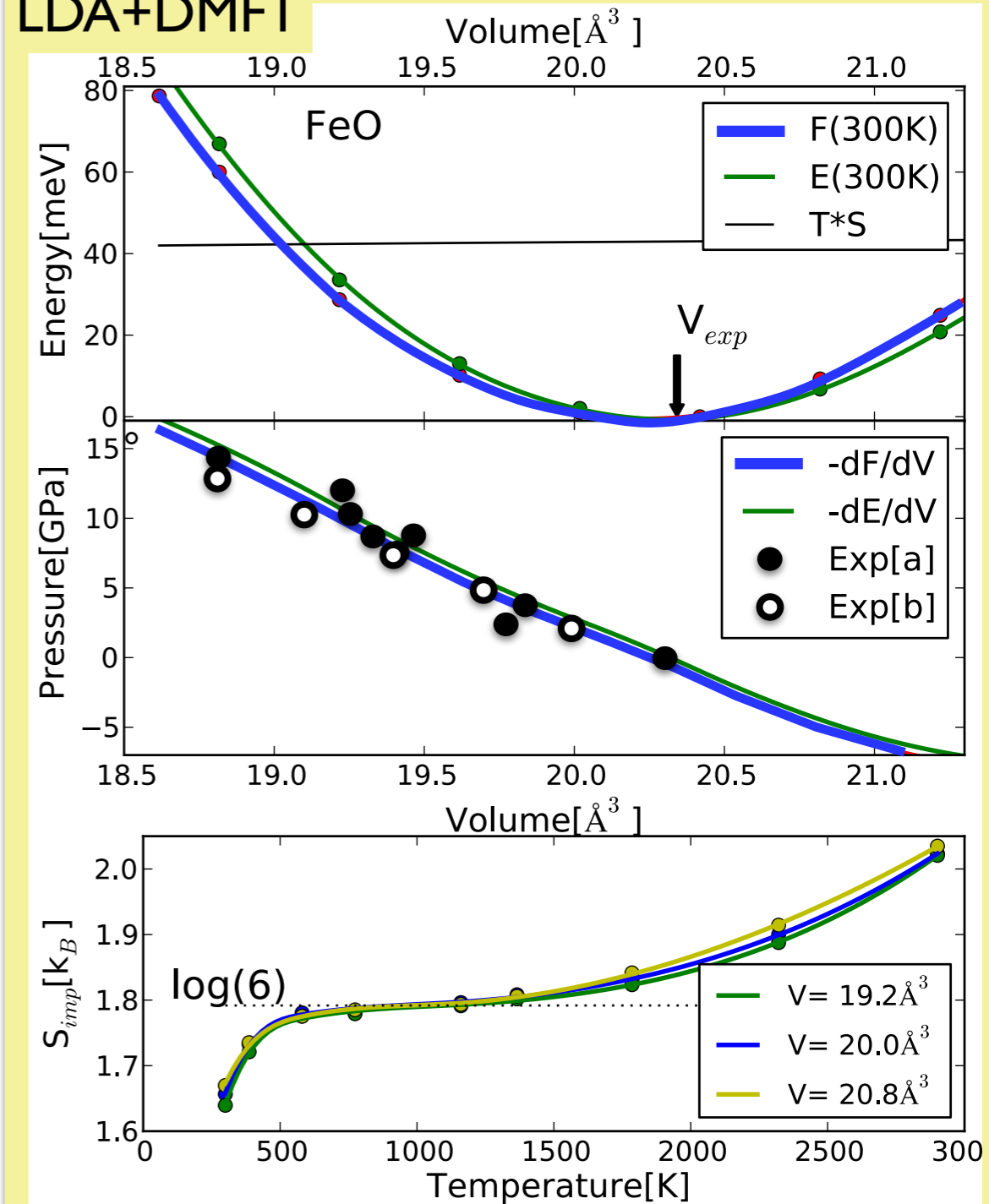


All DFT methods underestimate the volume (overbind) because of missing fluctuating moments. Ordered moments improve, but not good enough.

LDA+DMFT correct gap and volume.

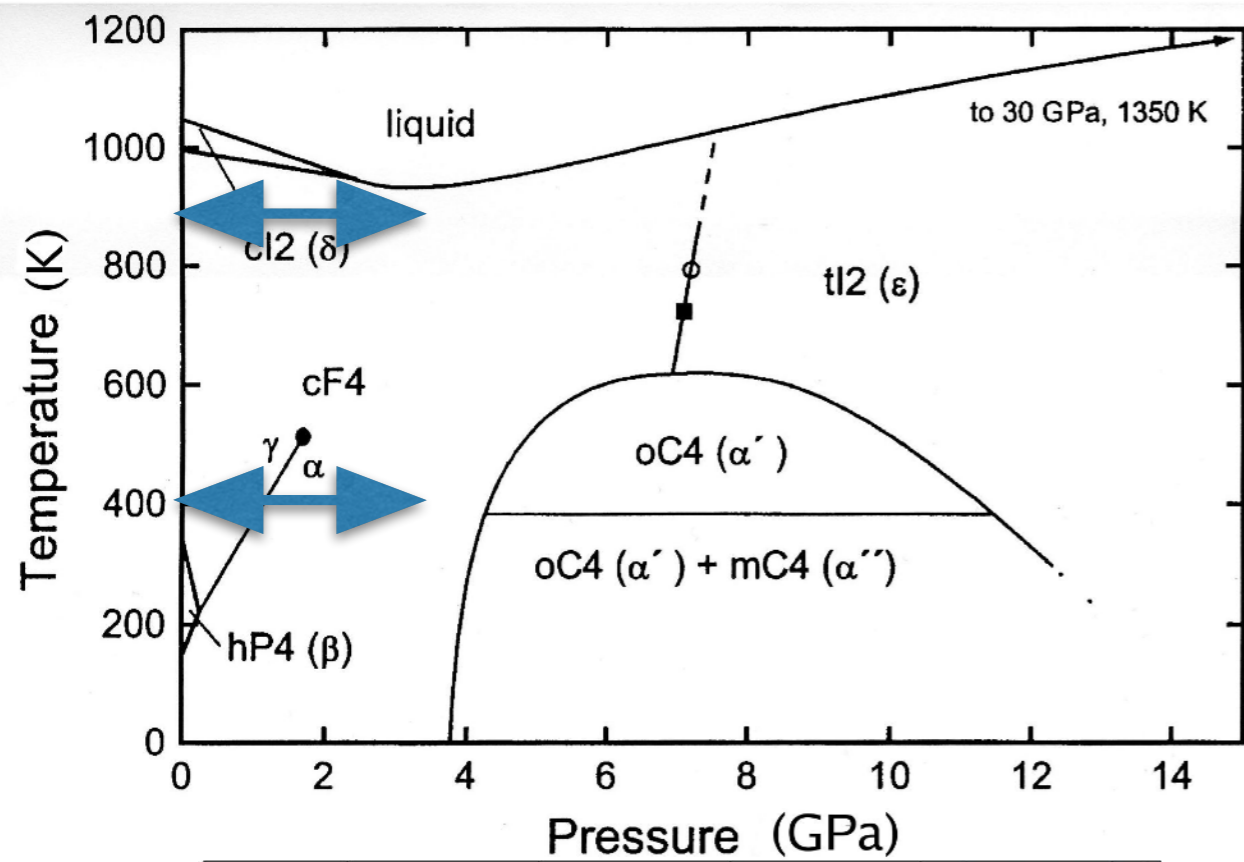
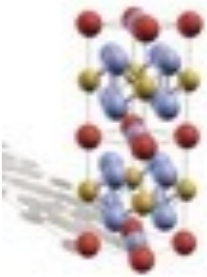


LDA+DMFT

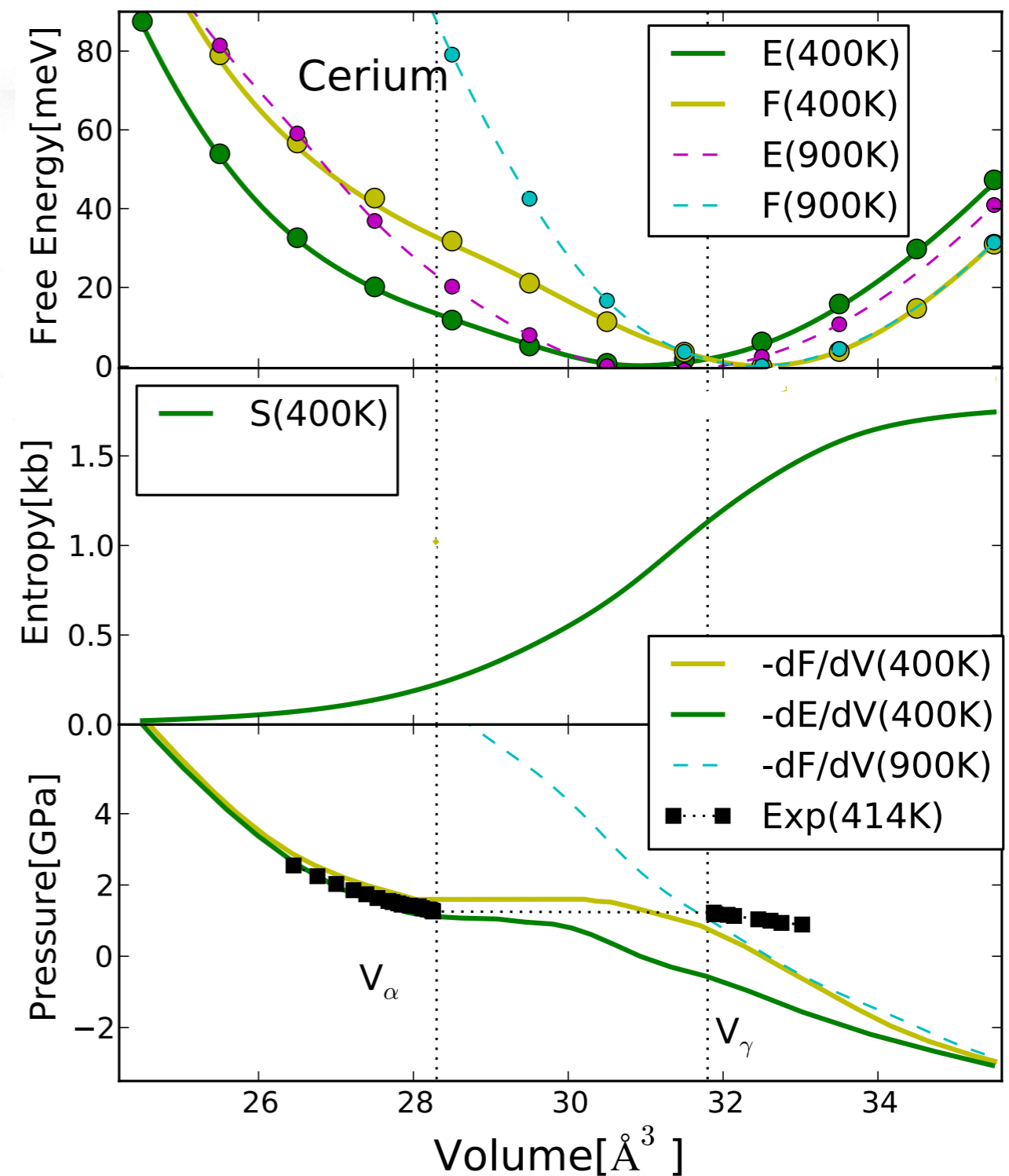


**Mott insulators and strongly correlated metals require non-perturbative treatment like DFT+DMFT.**

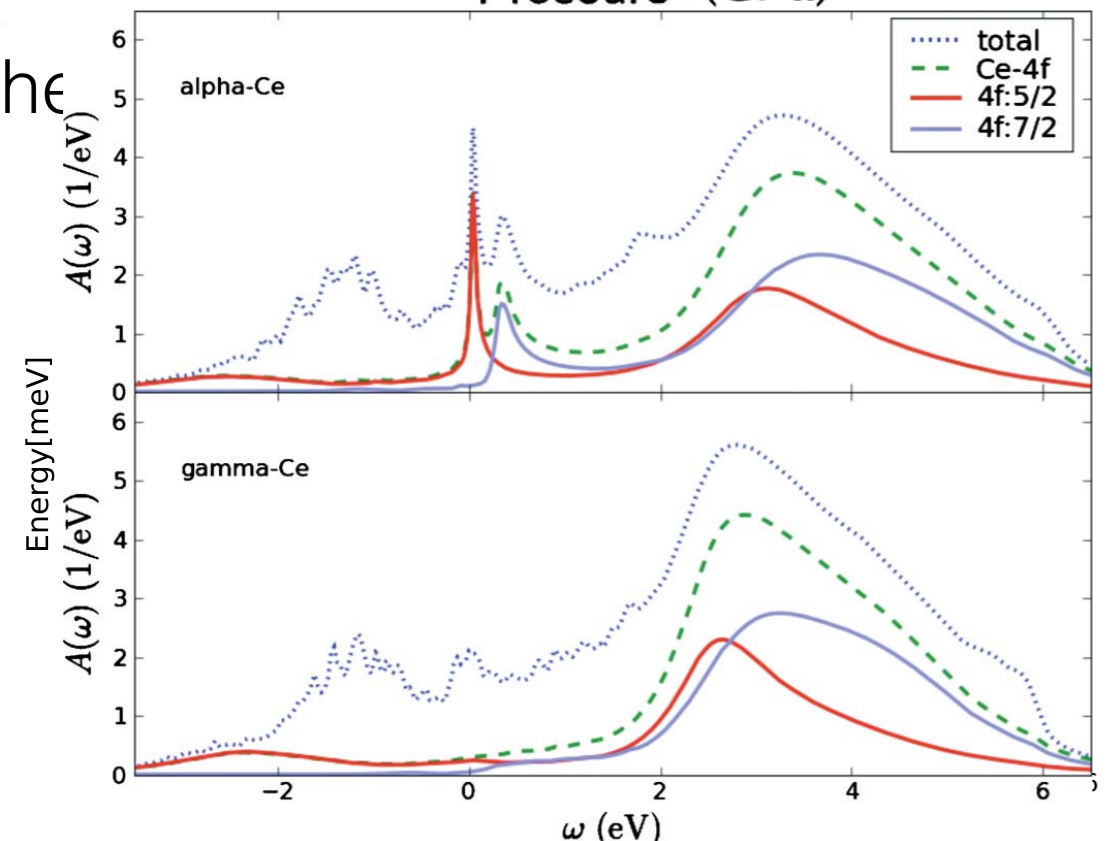
# Isostructural transition in elemental Cerium due to Kondo collapse mechanism



First order (entropy driven) transition



Other

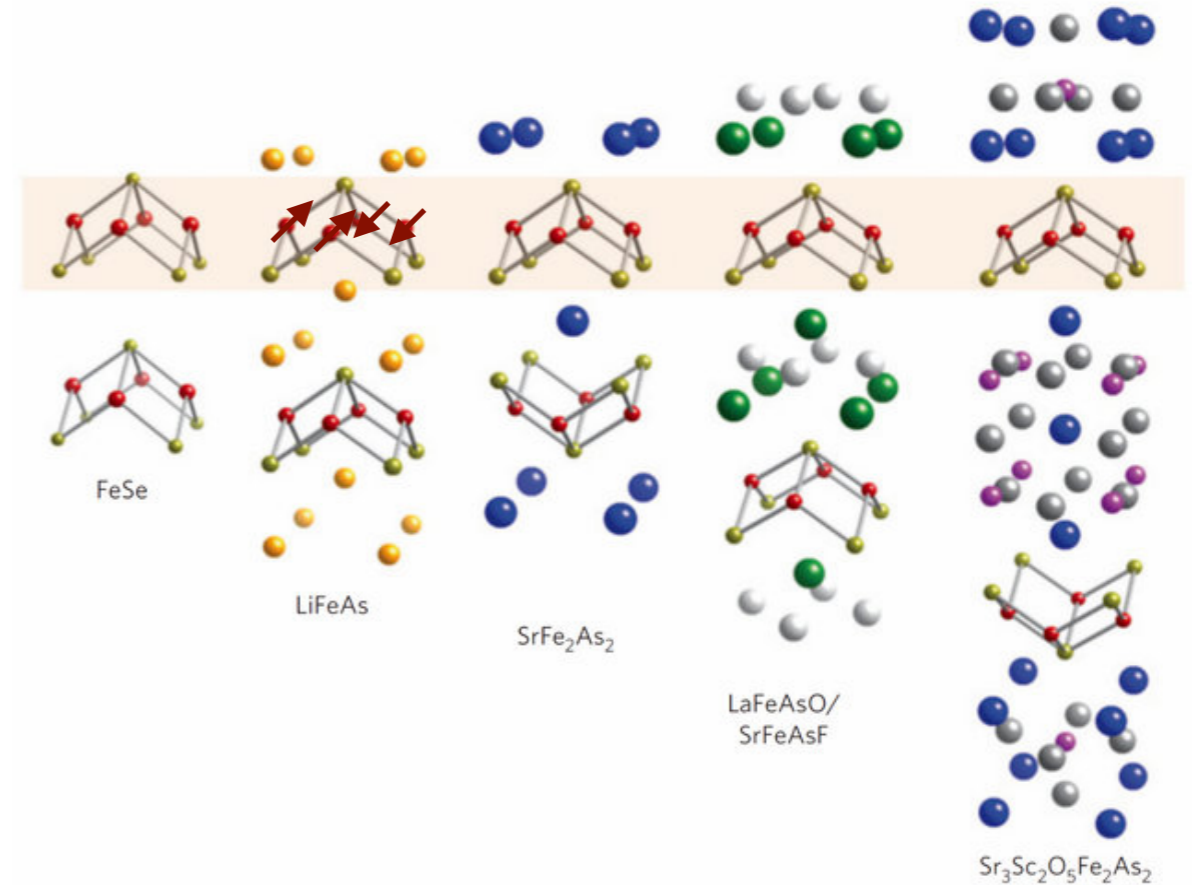
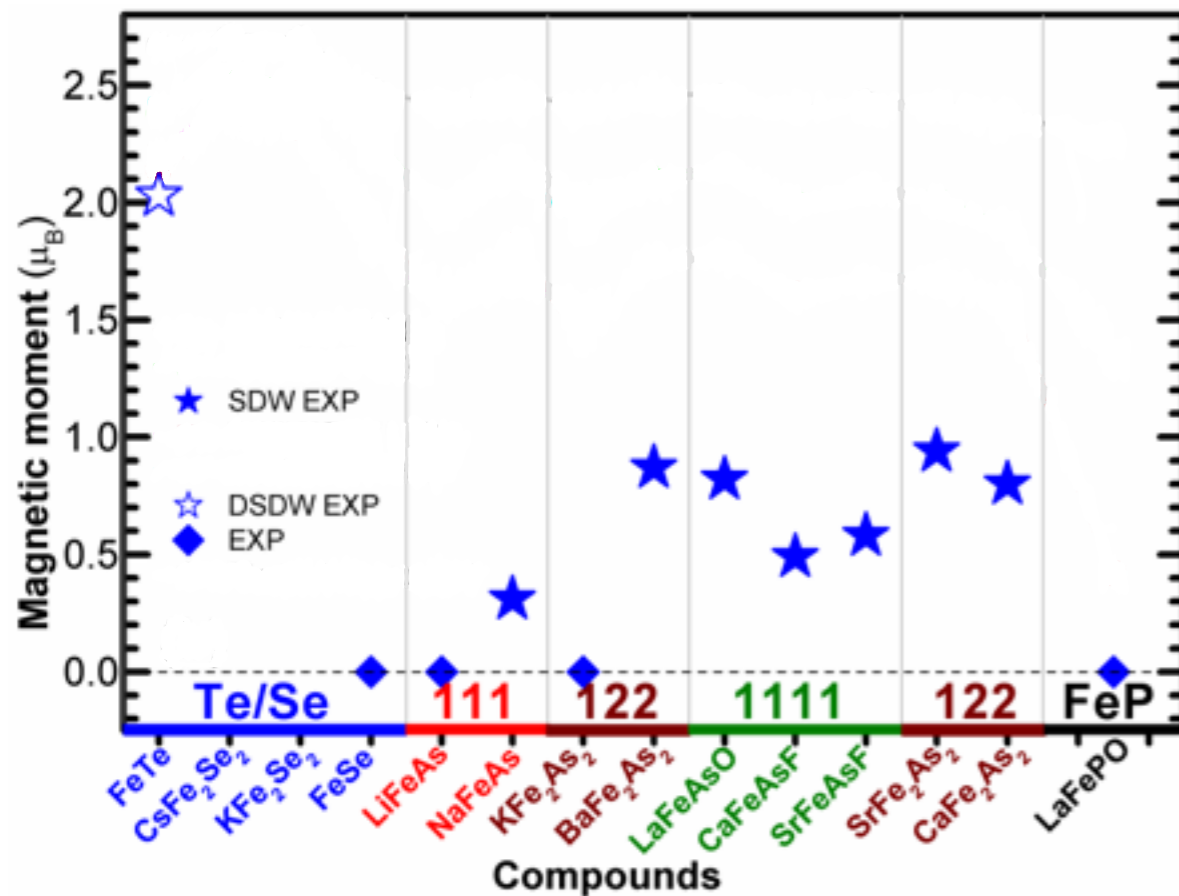


# Puzzle: Parent compounds of Fe SC have very different ordered magnetic moments

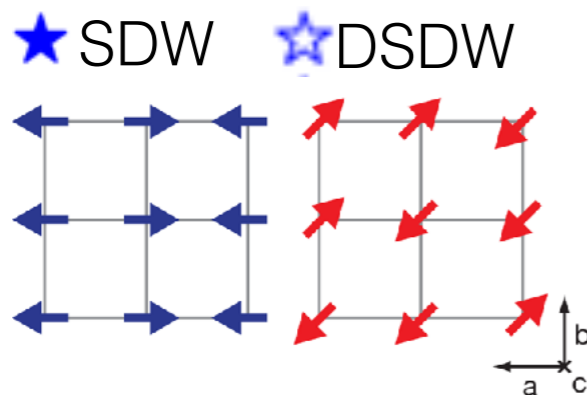
**Experiment: Ordered magnetic moments across many Fe superconductors**

no understanding what determines the size of the ordered moments

*many families of Fe superconductors share the same Fe-As tetrahedral unit*



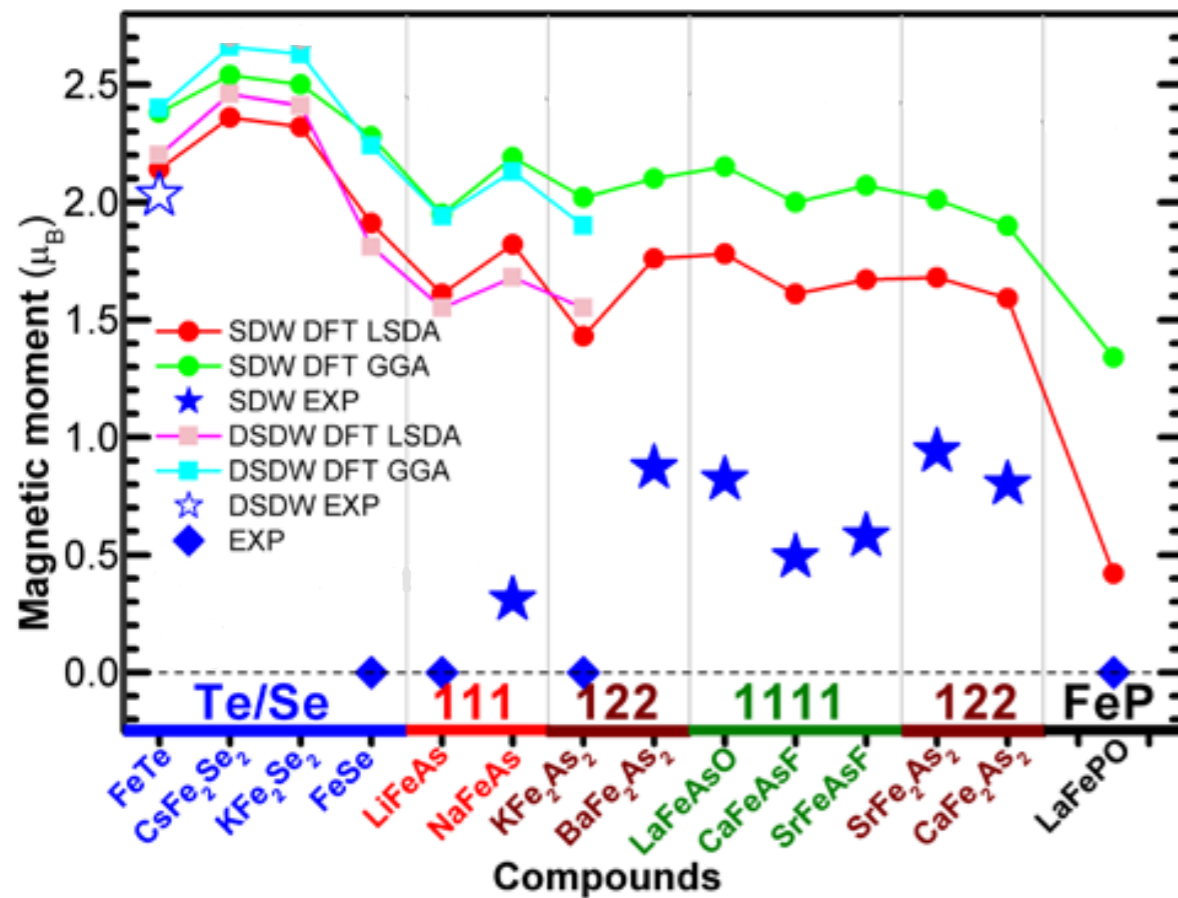
Contrast with cuprates, where the moments correspond to spin  $s=1/2$ .



What governs magnetism in Fe compounds?

# DFT does not predict well the moments

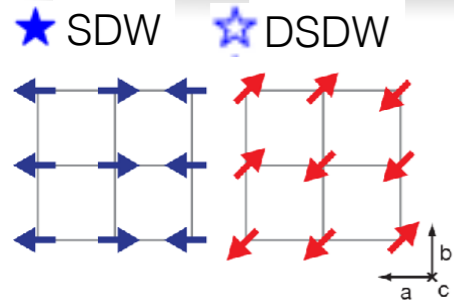
blue symbols : experiment  
green line: GGA, red line: LSDA



- DFT overestimates the ordered moment by roughly a factor of 2 (very uncommon)
- Many compounds appear magnetic in theory and non-magnetic in exp.



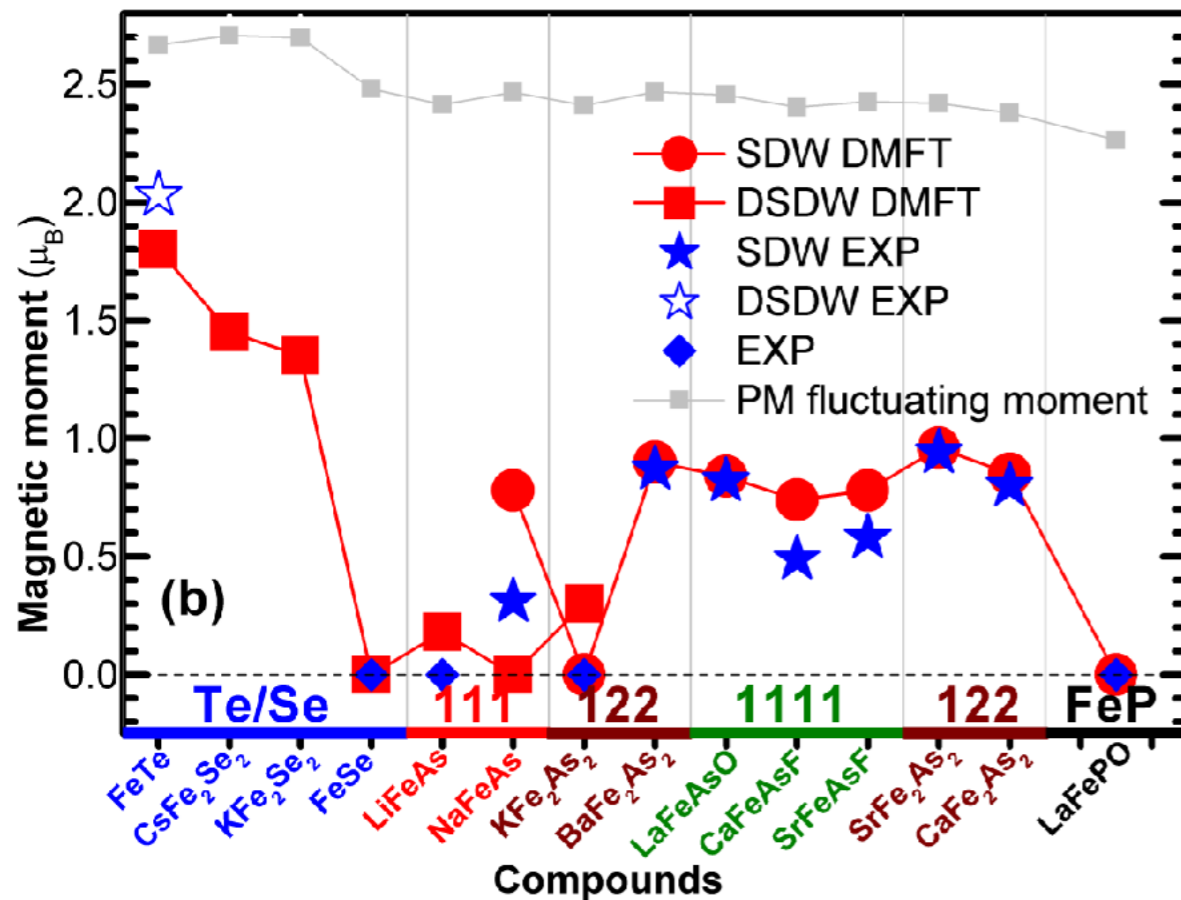
# DMFT predicted moments much closer to experiment



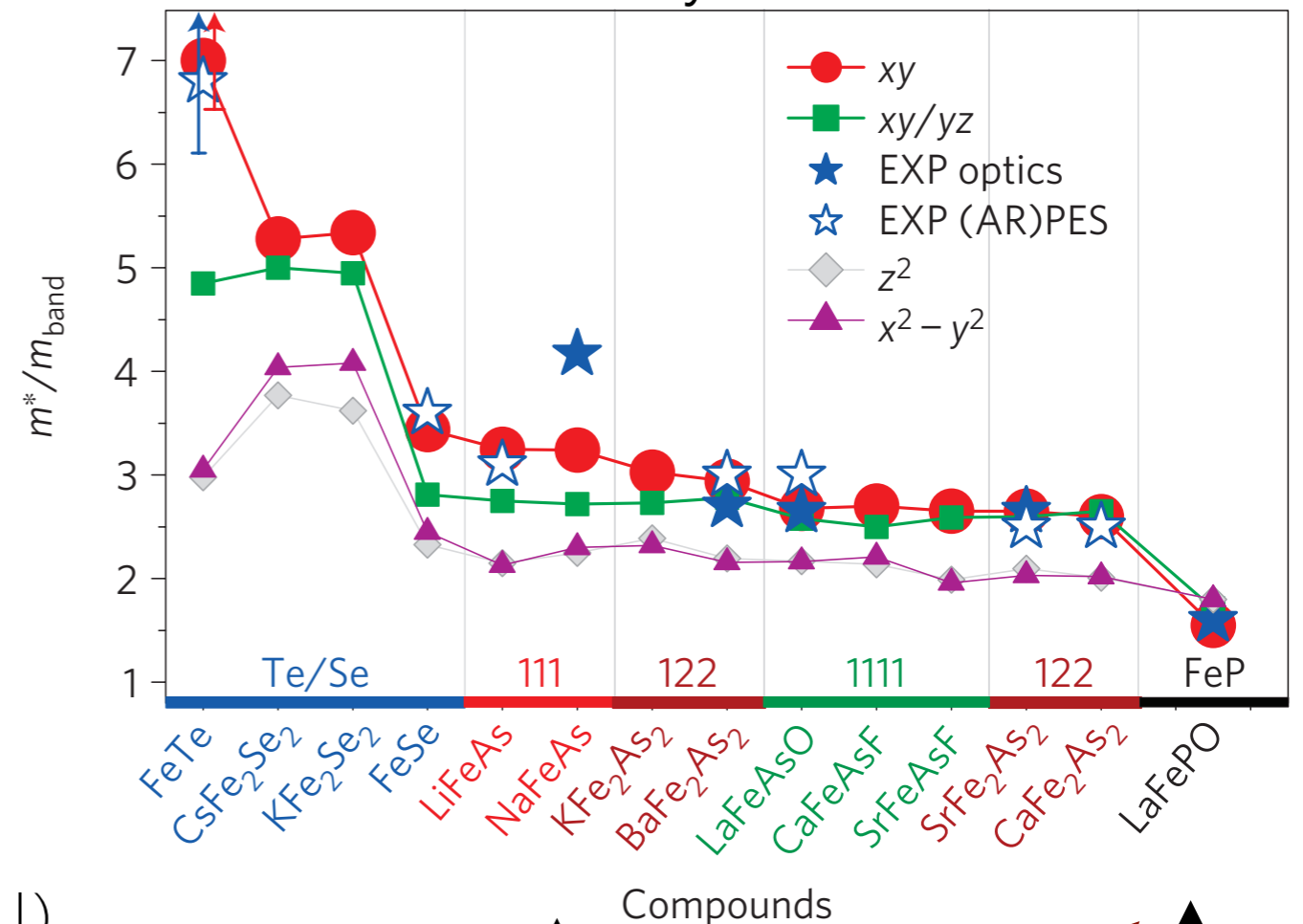
blue symbols : experiment  
red symbols : DFT-eDMFT

several competing effects:

- correlation strength ( $m^*$ ) (left versus right)
- competing ordered states (1,0),(0,1) with (1/2,1/2)
- substantial fluctuating moment remains in the ordered state

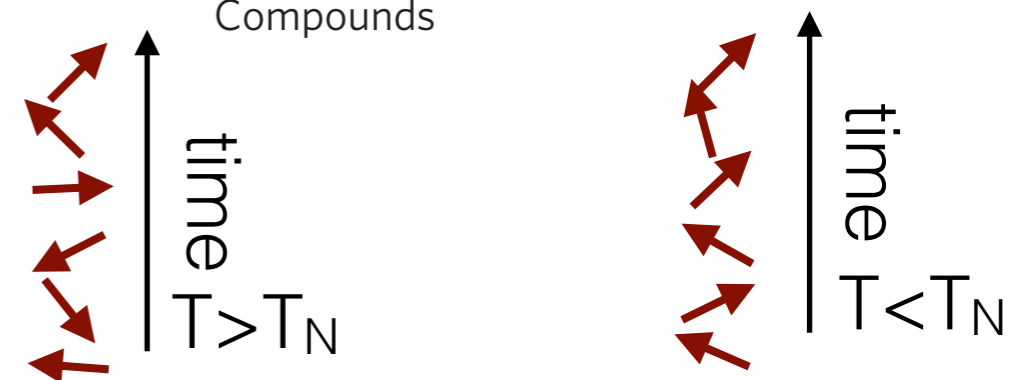


## electron mass beyond band-structure

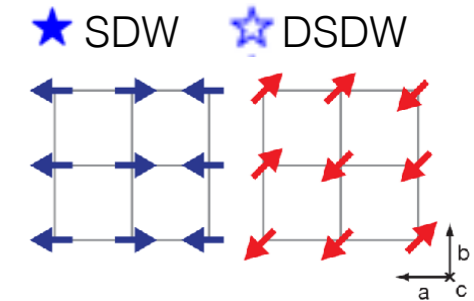


Yin, Haule & Kotliar, Nature Physics 7, 294-297 (2011).

*Prediction: large fluctuating moment ( $2-2.5\mu_B$ ) in para state  
Only a part of the fluctuating moments orders.*



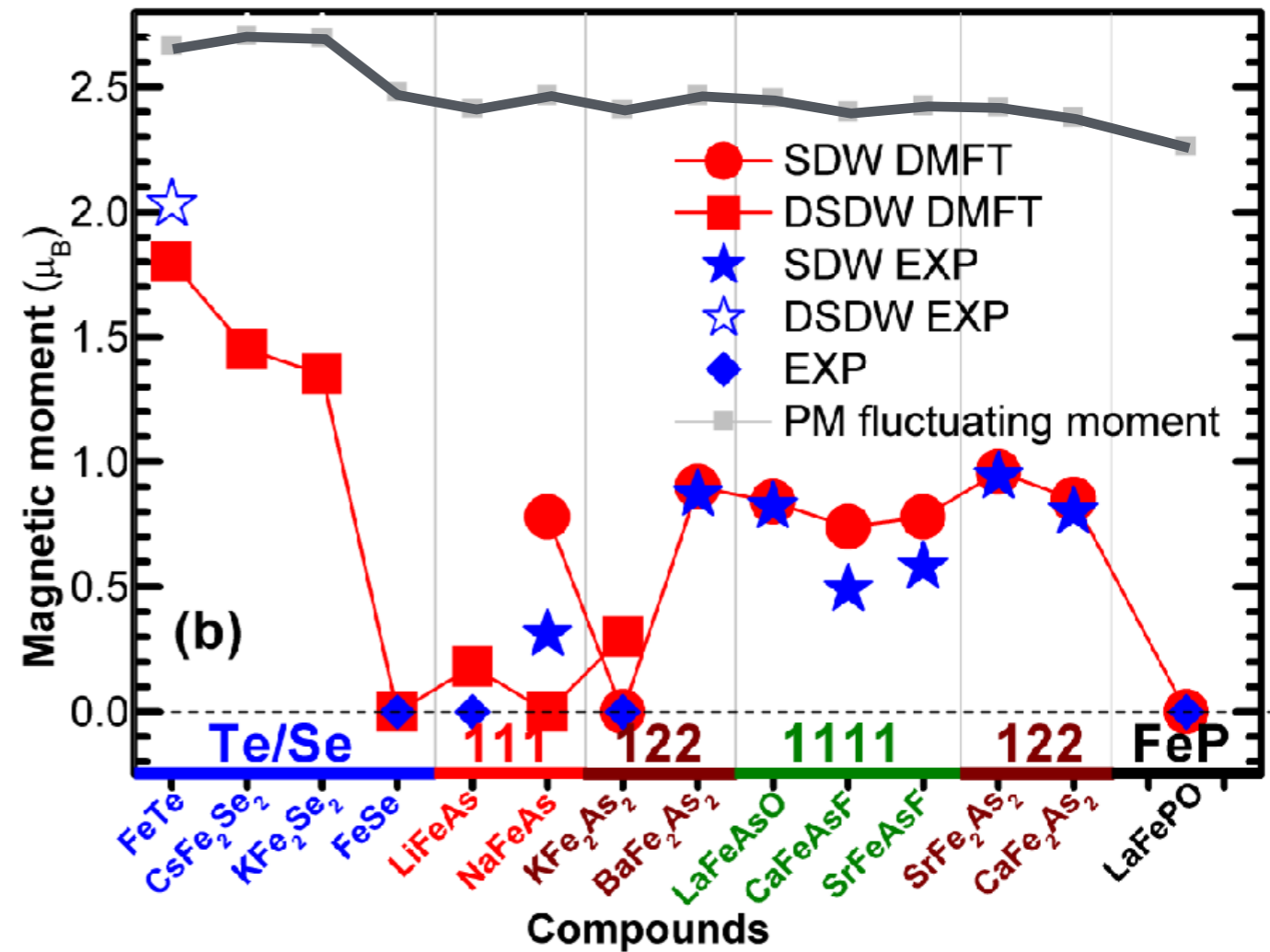
# DMFT predicted magnetic moments in Fe-superconductors



blue symbols : experiment  
red symbols : DFT-eDMFT

Can distinguish between the fluctuating moment  $\langle S^2 \rangle$ , and the ordered moment  $\langle S \rangle^2$ . In para  $\langle S \rangle = 0$  on each site.

Substantial fluctuating moment remains in the ordered state

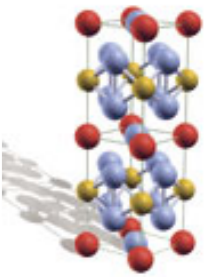


Yin, Haule & Kotliar, Nature Physics 7, 294-297 (2011).

Prediction: large fluctuating moment ( $2-2.5\mu_B$ ) in para state  
Only a part of the fluctuating moments orders.

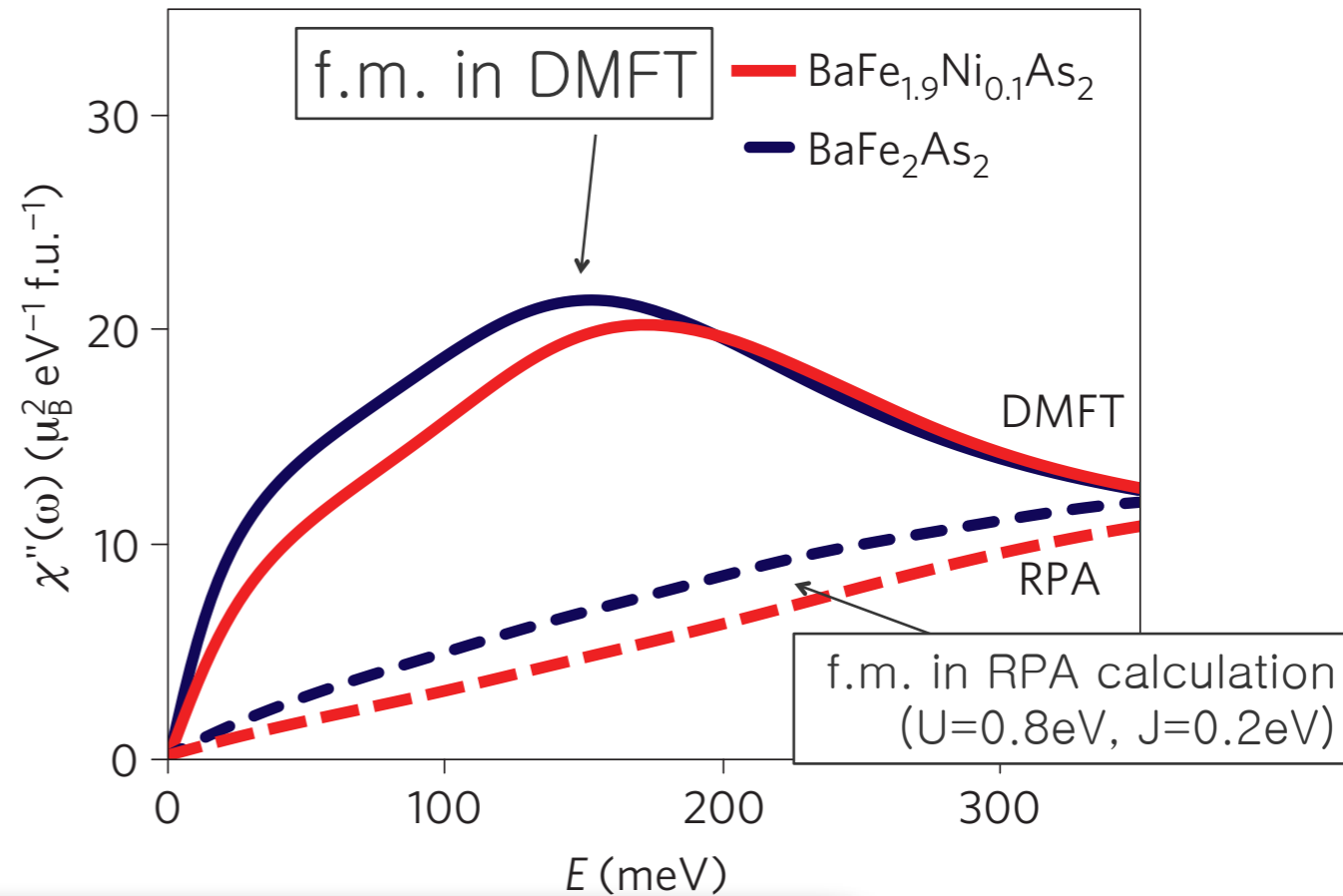
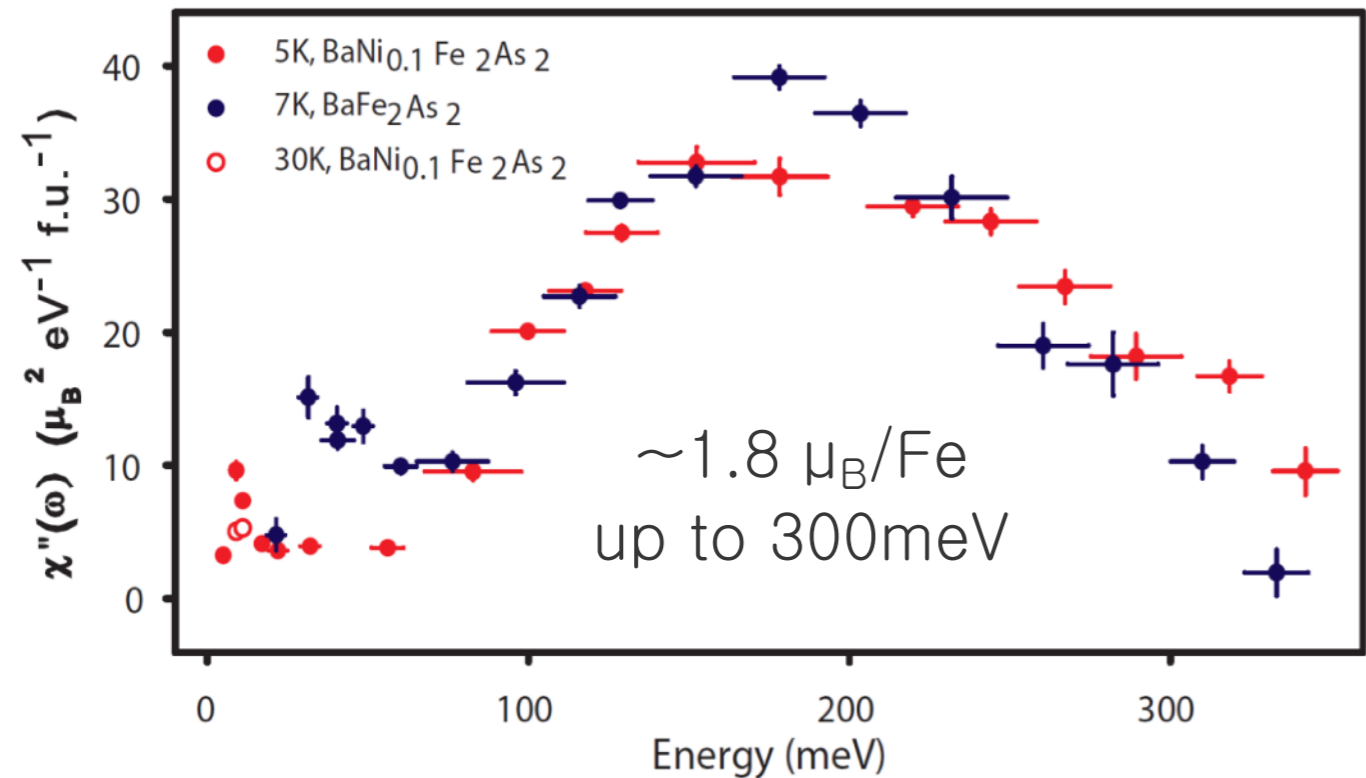


# Predicted large fluctuating moment confirmed



Fluctuating moment measured by neutrons – integral of local susceptibility:

$$\langle \mu^2 \rangle = \int \frac{d\omega}{\pi} n(\omega) \chi''(\omega)$$



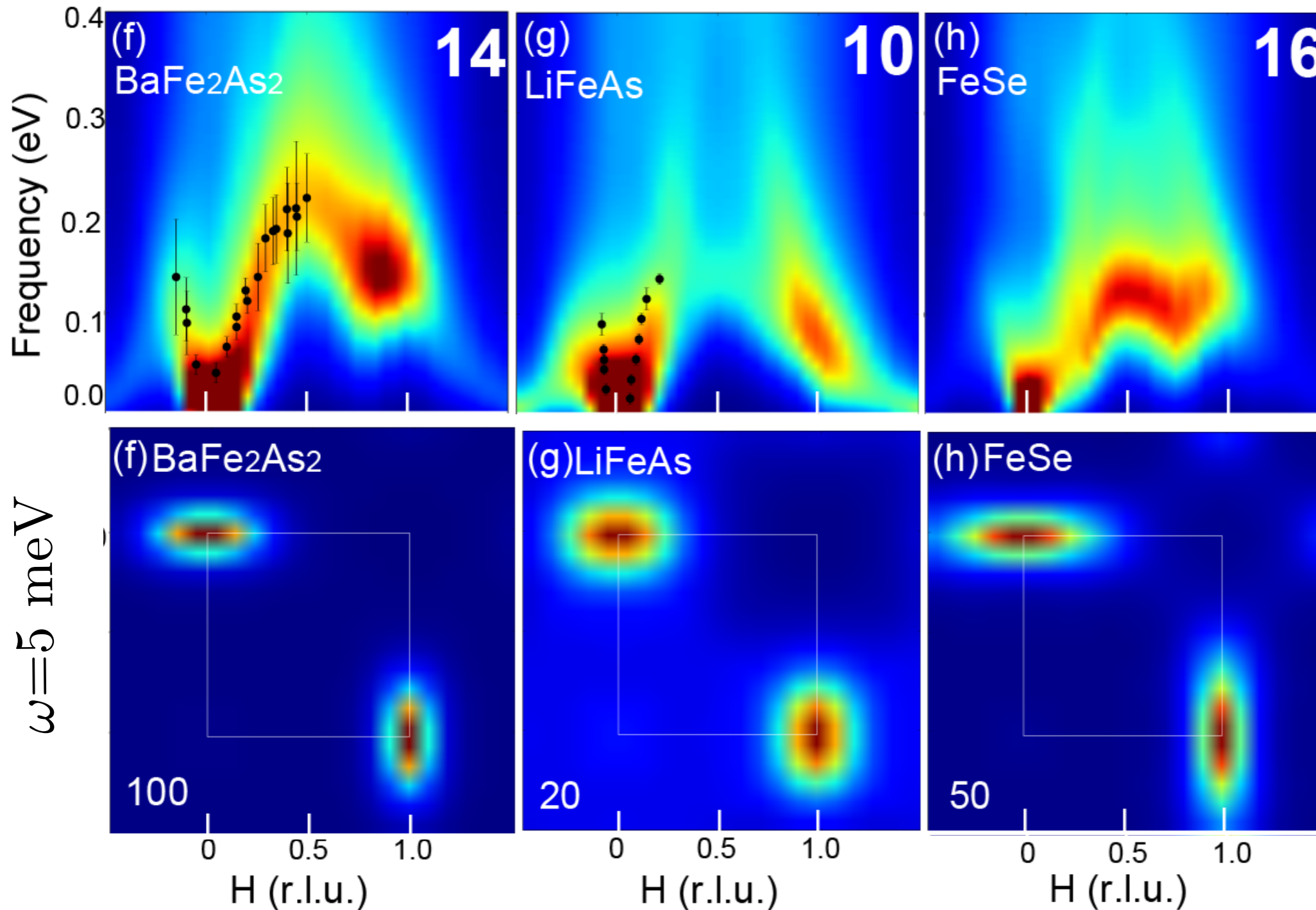
Large fluctuating moment can not be explained by a purely itinerant model - property of Hundness!

The DMFT account for a dual nature of electrons in Hund's metals: itinerant and localized nature.

# magnetic susceptibility in paramagnetic state

black dots : inelastic neutron scattering

color : DFT-DMFT paramagnetic spin susceptibility



Magnetic susceptibility is the only quantity up to now which requires the two particle correlation function.

It is harder to compute.

**DMFT can predict well neutron dynamical SF**

# Electron-phonon coupling in fluctuating moment systems

In Fe-SC electron-phonons coupling is too weak to explain high  $T_c$ 's.

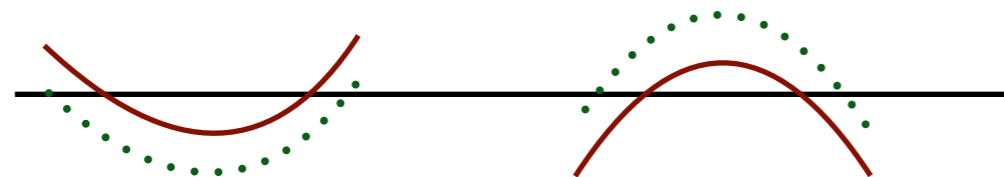
K. Haule, J. H. Shim, G. Kotliar, *Phys. Rev. Lett.* 100, 226402 (2008)

L. Boeri, O.V. Dolgov, and A. A. Golubov, *PRL* 101, 026403 (2008).

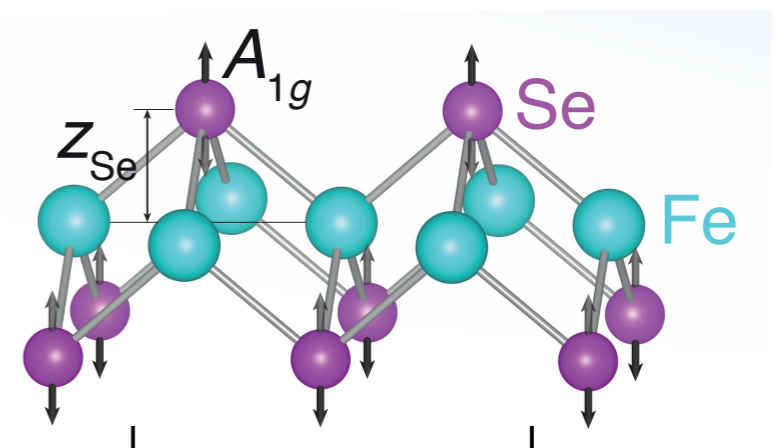
Nevertheless, phonons can boost  $T_c$  when cooperating with unconventional spin-mediated (correlation-driven) superconducting mechanisms.

The phonon enhancement of  $T_c$  is determined by electron-phonon coupling:

Change of the band structure due to displacement of the ions in the direction of a phonon mode.

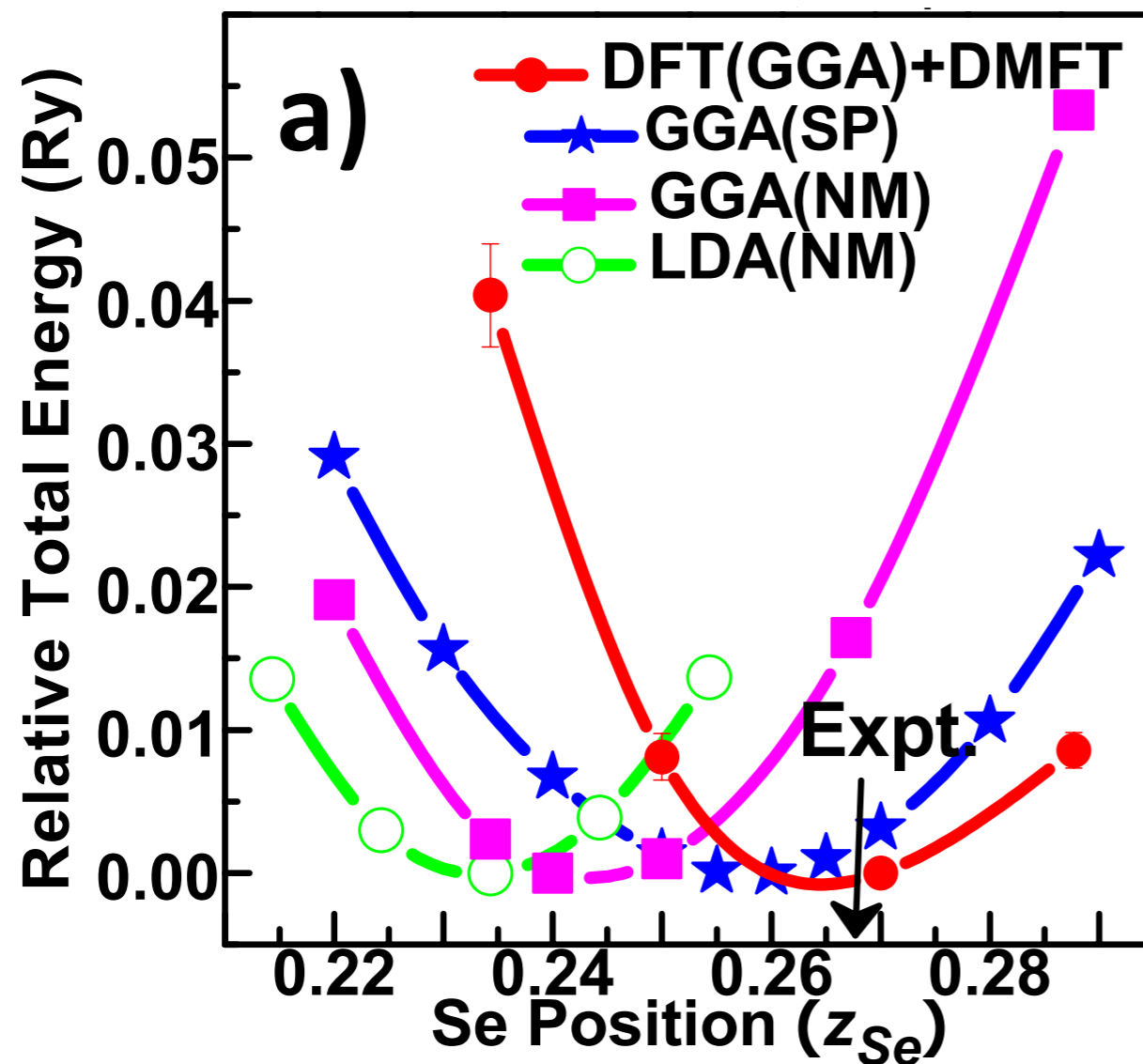


— before displacement  
..... after displacement



# Ion positions in fluctuating moment systems

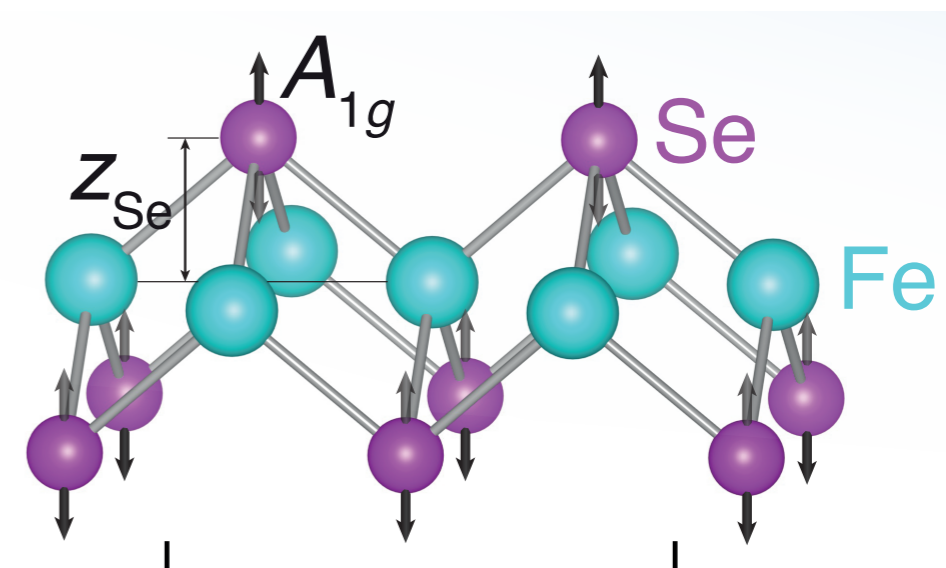
The vertical distance between Fe and Se atoms by different theories



DFT+DMFT Prediction: **Subhasish Mandal**, Cohen, & Haule, PRB **89**, 220502(R) (2014).

Correlation on Fe ion push away other ions (Se).

electrons in correlated orbitals need more space

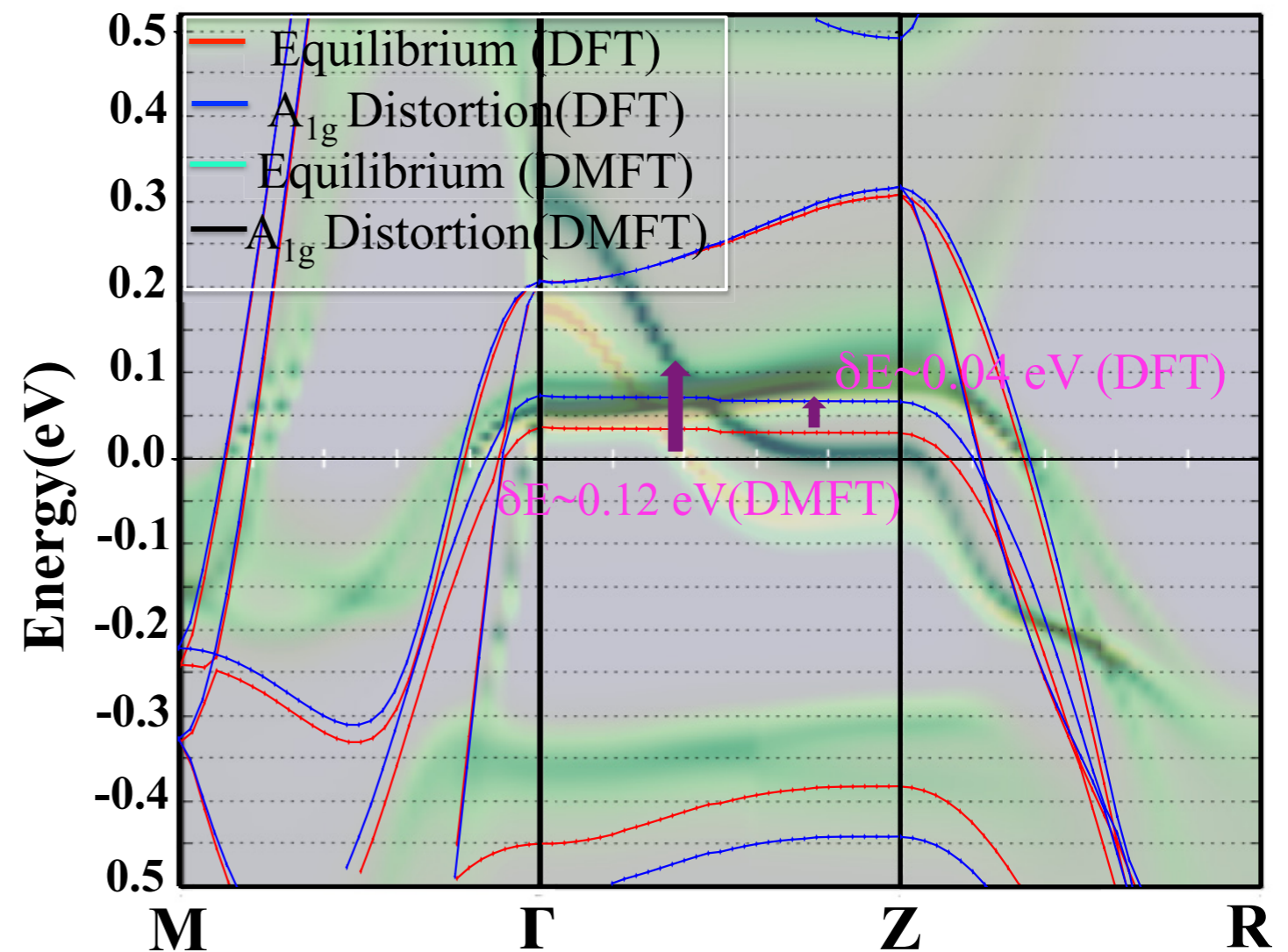
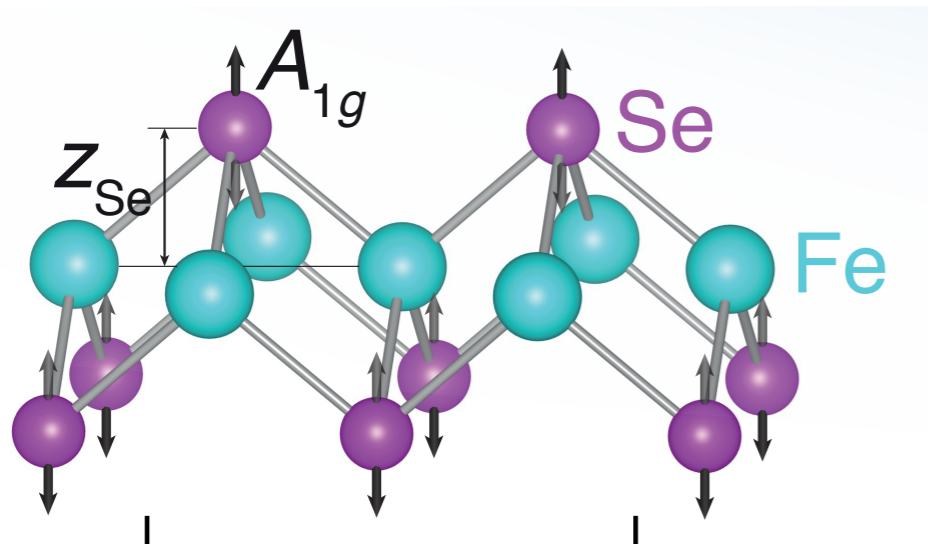


# Electron-phonon coupling in fluctuating moment systems

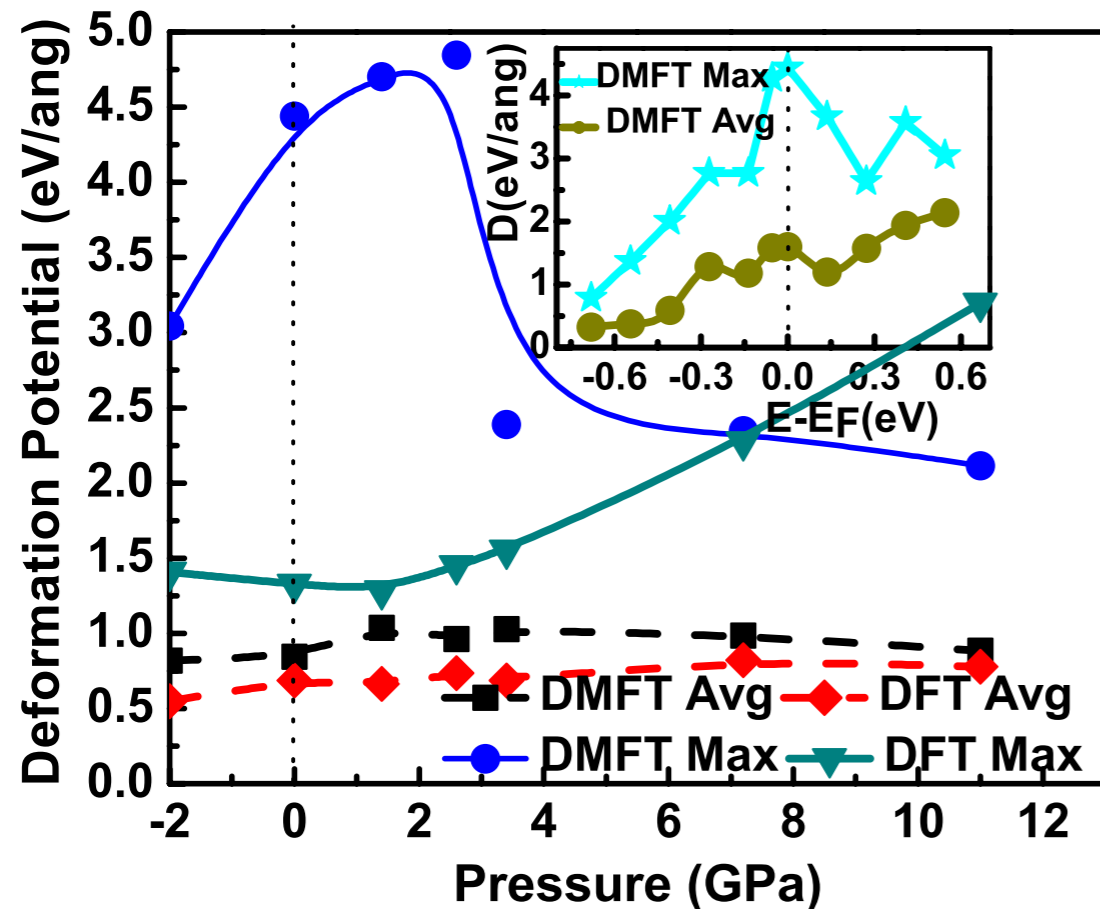
*The DMFT electronic states are much more sensitive to Se displacement than predicted by DFT.*

*Can be understood as a feedback effect of correlations on electrons through structure.*

*Correlations push Se away from Fe, which reduces hybridization strength of Fe with Se, which increases correlations, and push Se further away (Kondo coupling exponentially sensitive to hybridization)*



# Electron-phonon coupling in FeSe



- *Pressure dependence tracks  $T_c$  of FeSe*
- *Phonons boost SC in FeSe*
- *eDMFT suggests up to one order of magnitude stronger e-ph coupling than DFT (A<sub>1g</sub> mode)*

DFT+eDMFT Prediction:  
Mandal, Cohen, & Haule, PRB **89**, 220502(R) (2014).

position of Se

$z_{\text{Se}}(\text{r.l.u.})$

DFT

DFT+eDMFT  
(2014)

Experiment

A<sub>1g</sub> frequency

$f_{\text{A}_{1g}}(\text{THz})$

$6.5 \pm 0.3$

5.7

e-ph coupling

$\Delta E_{xz/yz}/\Delta z_{\text{Se}}(\text{meV/pm})$

$-1.6 \pm 0.2$

-10.3 to -13.4

0.2456

0.27

0.2653



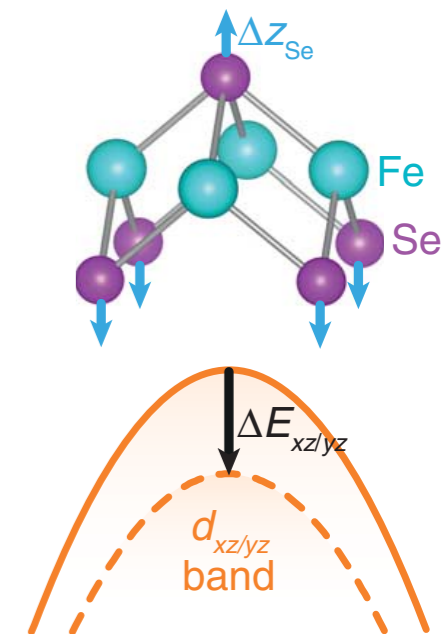
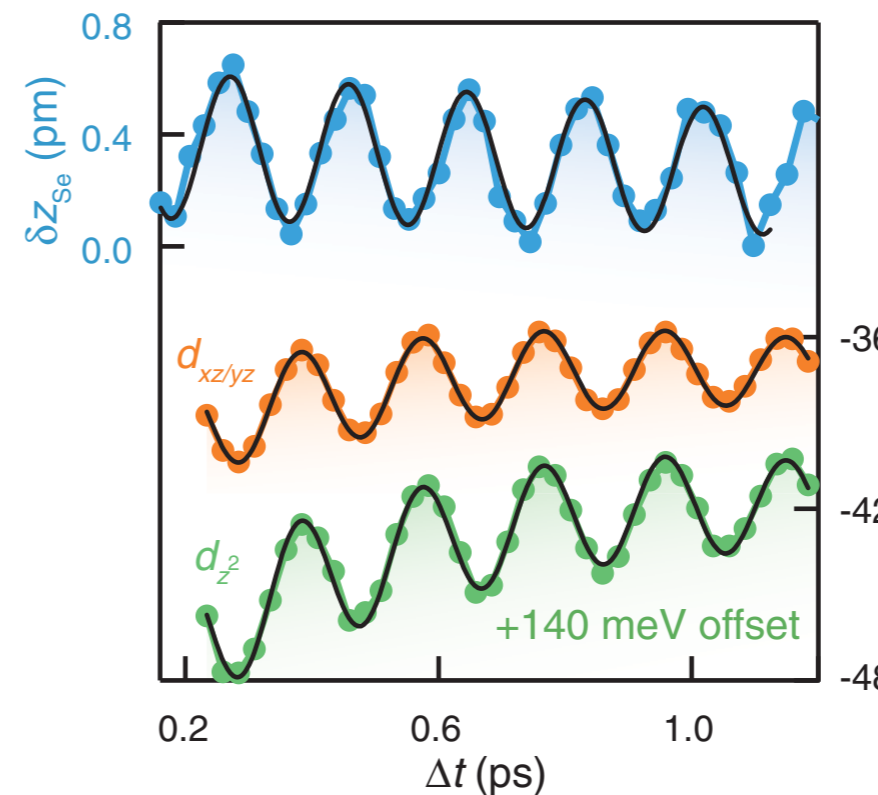
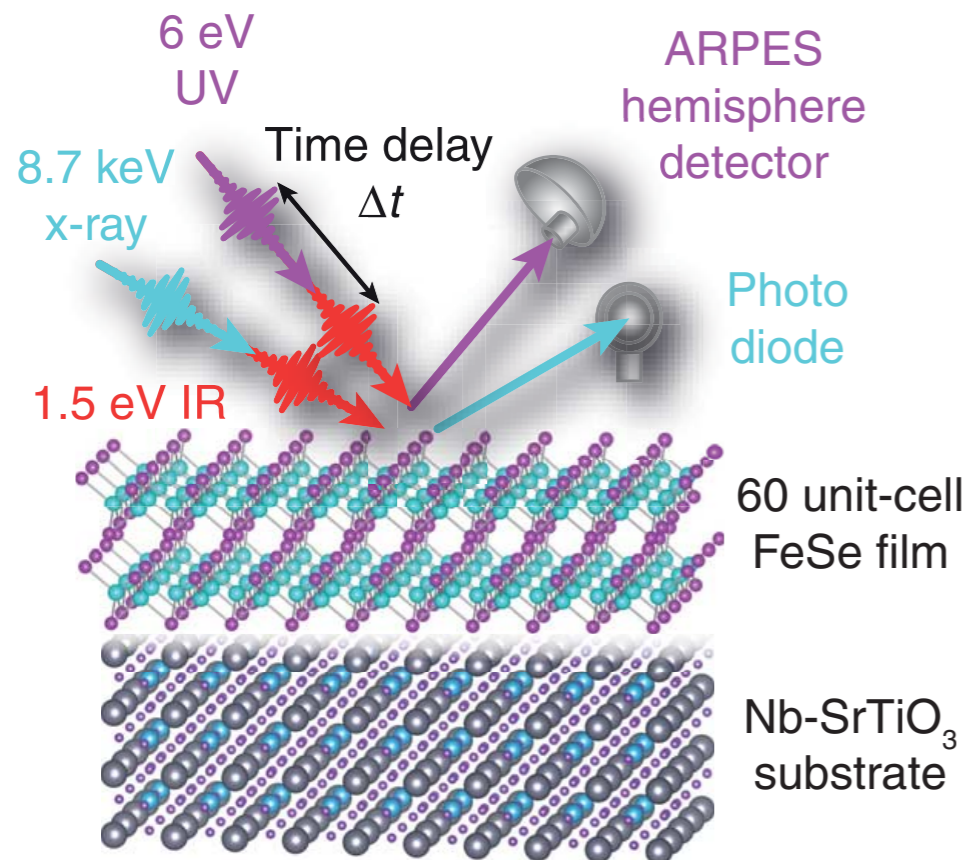
# Stanford pioneering exp: direct measurement of e-ph c.

send IR pump pulse to excite A<sub>1g</sub> phonon

measure time resolved X-ray  
measure time resolved ARPES

Bragg peak position is oscillating with A<sub>1g</sub> phonon frequency

Bands are oscillating with the same frequency.



DFT+eDMFT Prediction:

Mandal, Cohen, & Haule, PRB **89**, 220502(R) (2014).

Experiment:

S. Gerber, ..., Z.X. Shen et.al., Science 357, 71 (2017).

position of Se

$z_{\text{Se}}$ (r.l.u)

DFT  
0.2456

DFT+eDMFT  
(2014)  
0.27

Experiment  
(2017)  
0.2653

A<sub>1g</sub> frequency

$f_{\text{A}_{1g}}$ (THz)

$6.5 \pm 0.3$

5.7

$5.30 \pm 0.05$

e-ph coupling

$\Delta E_{xz/yz} / \Delta z_{\text{Se}}$ (meV/pm)

$-1.6 \pm 0.2$

-10.3 to -13.4

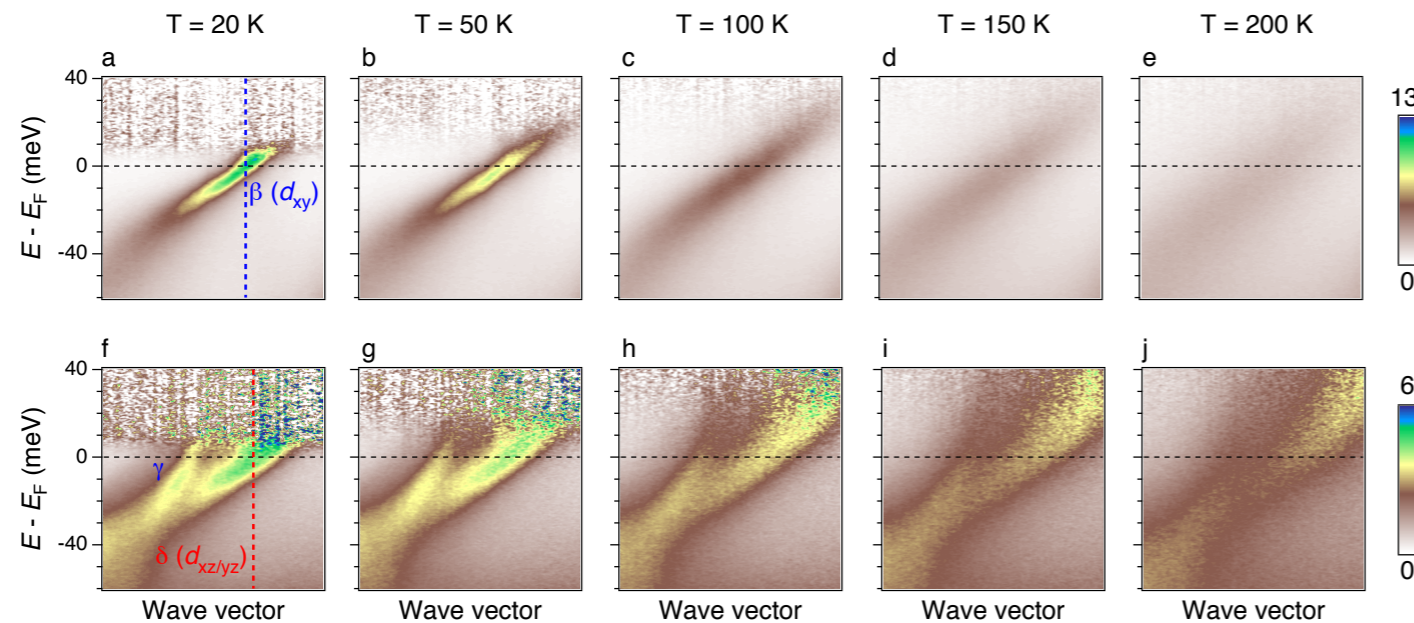
$-13.0 \pm 2.5$

**Direct confirmation of DFT+eDMFT prediction**

# Bands in the presence of fluctuating moments

## Momentum resolved spectra of LiFeAs

### ARPES

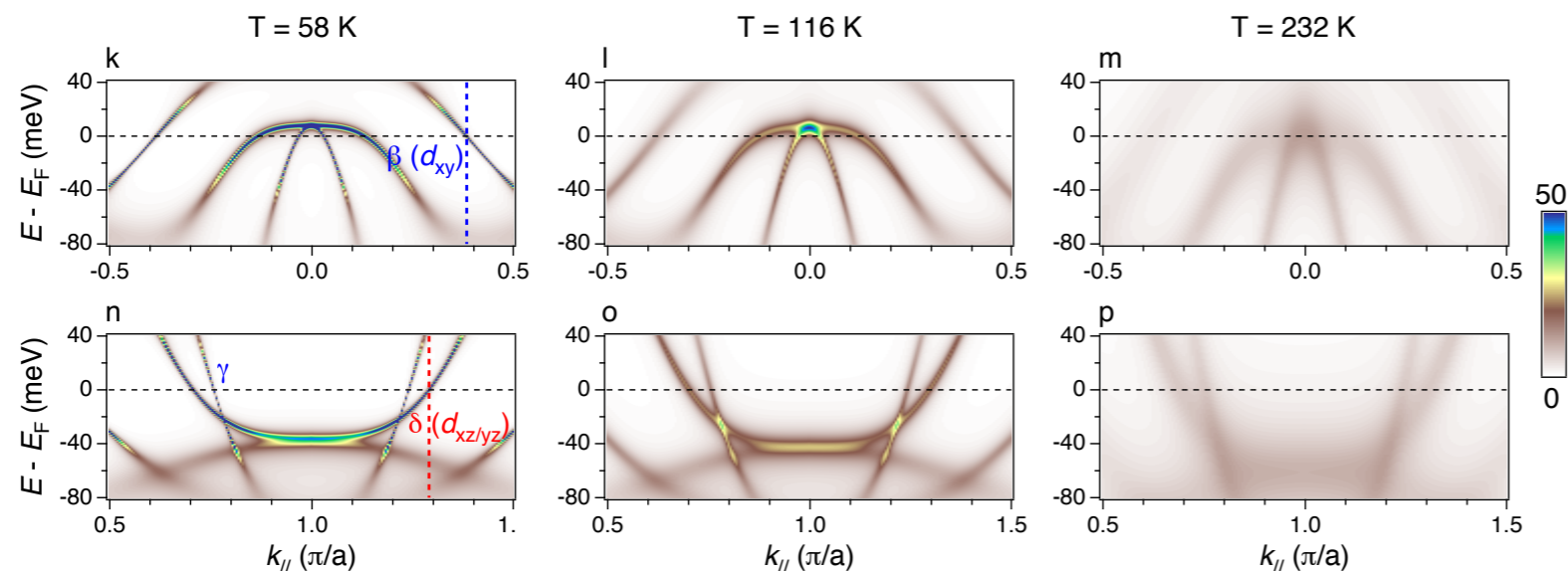


Bands are sharp only very near the fermi level and only at low temperature (Fermi liquid).

Above the coherence temperature, electrons are better described as fluctuating moments, rather than plane waves.

$$m^*/m \sim 3$$

### DFT+DMFT for LiFeAs:

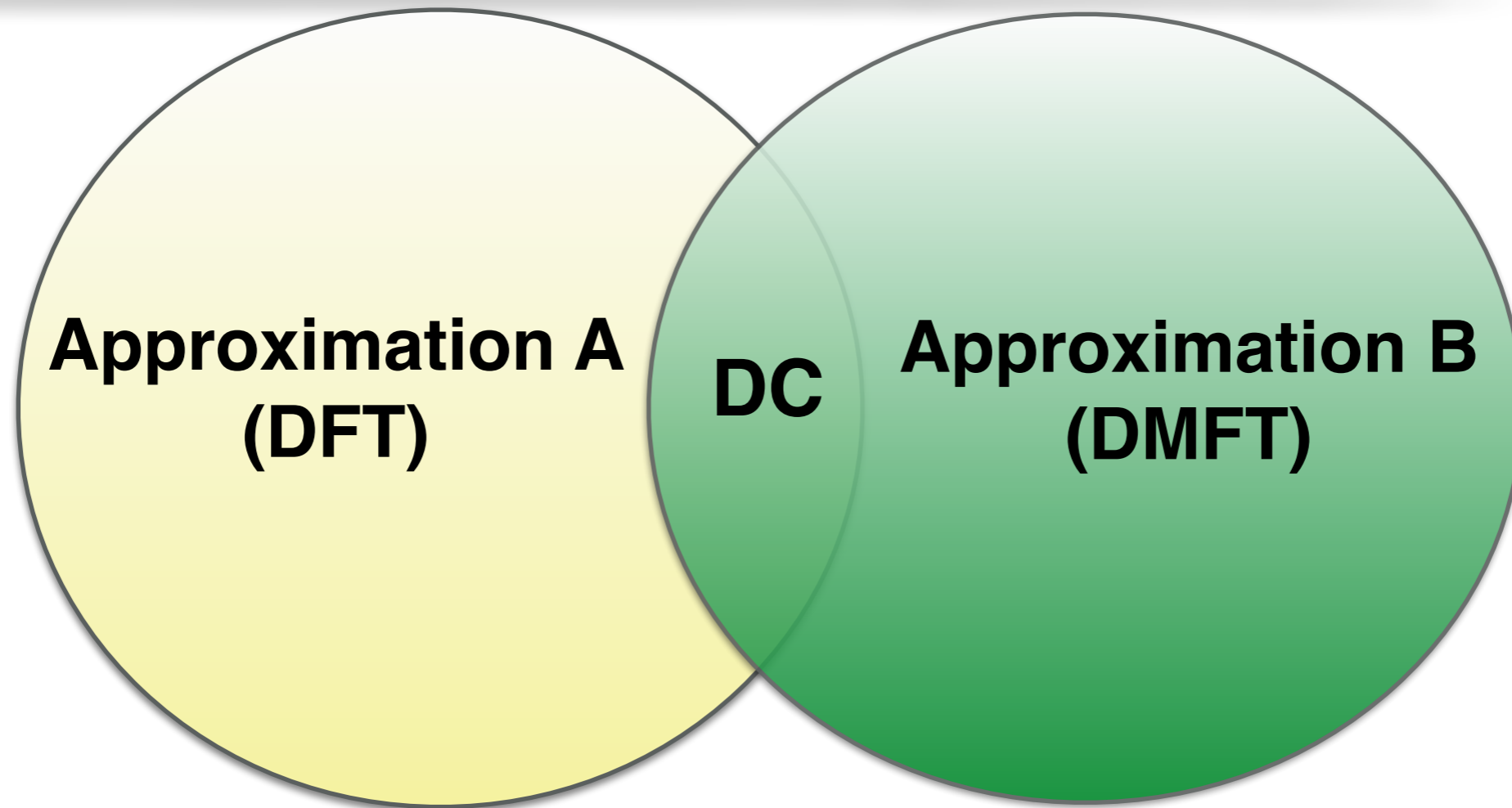


DMFT predicted coherence incoherence crossover in Fe-SC (Hund's metals)

(Haule & Kotliar NJP 11, 25021 (2009) )

# Double-Counting

---



Some part of exchange/correlations counted in both approximations.

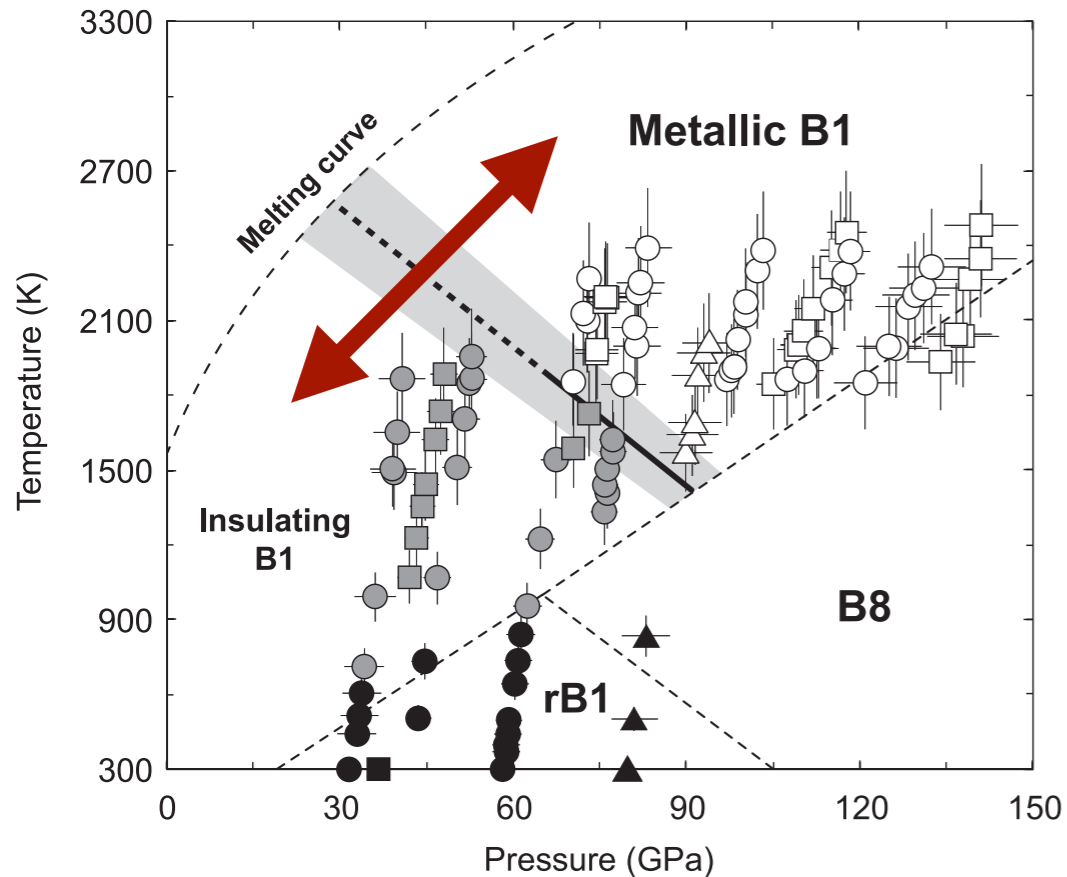
**Important : Determines the oxidation state of correlated ion**

*only a degenerate Hubbard model approximation can “avoid” this problem*

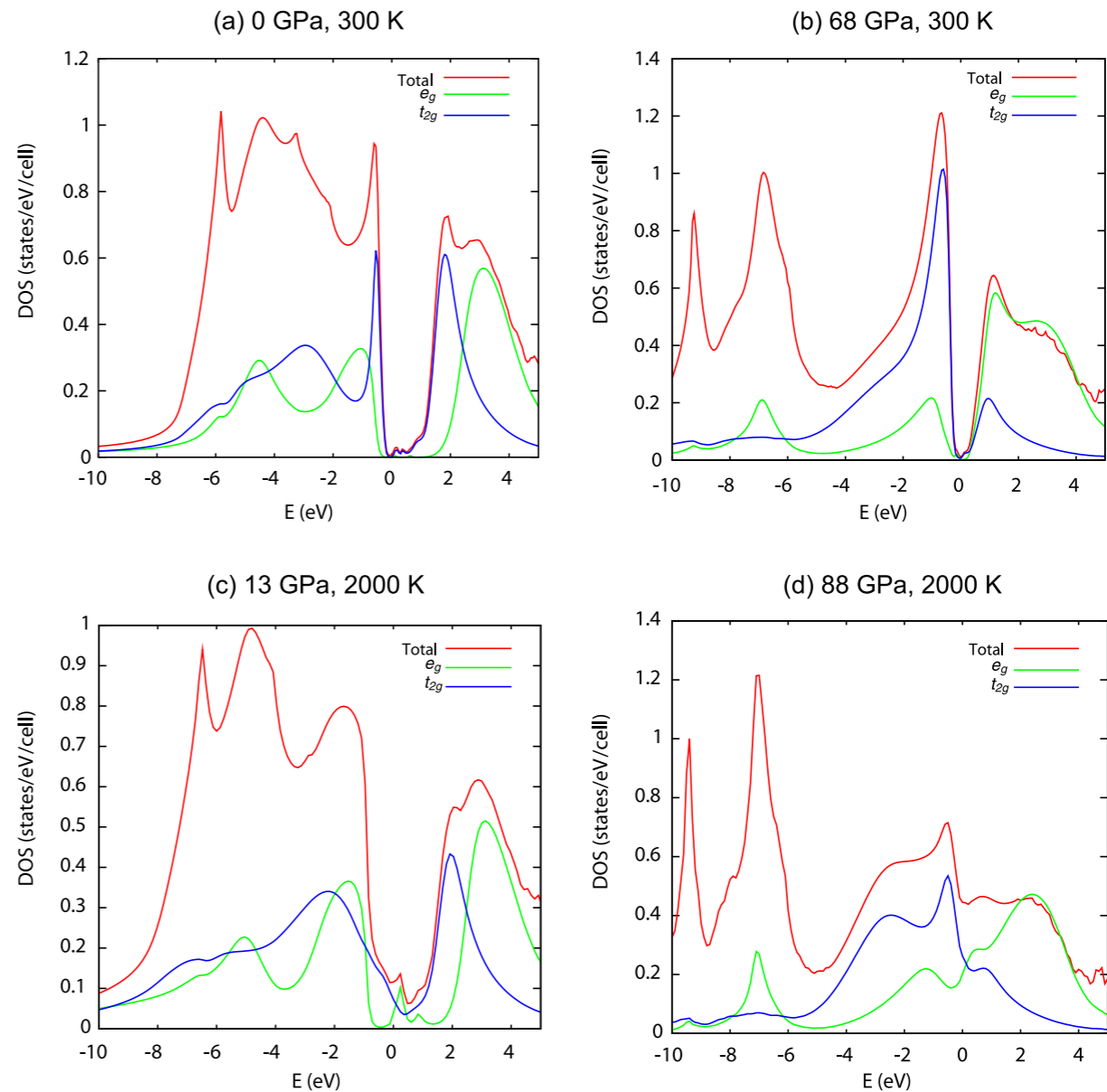
# Metal-insulator transition in FeO (earth core)

High-spin to low spin transition occurs only in correct  $d^6$  valence state of iron.

high-spin : insulator  
low spin : metal



**Isostructural MIT in FeO predicted by DFT-DMFT theory.**



**DMFT predicted MIT in FeO**

*Kenji Ohta, R. E. Cohen, et.al., PRL 108, 026403 (2012)*

# Importance of correct valence in $\text{RNiO}_3$

P21/n  
insulating

## Basic physical picture:

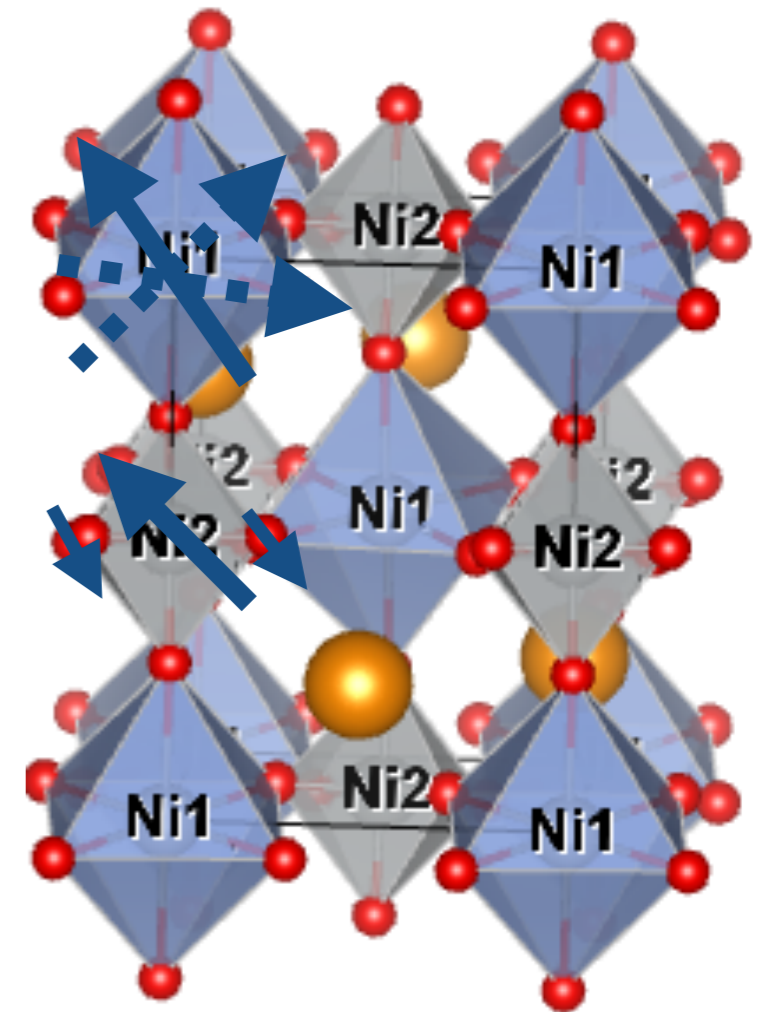
The chemical picture suggest Ni  $d^7$  configuration.

**Bond disproportionation:**  $\text{Ni}_1$  is in  $d^8$  with  $S=1$  while  $\text{Ni}_2$  + two ligand holes  $d^8L_2$  with total  $S=0$ .

**S=1**

fluctuating m.

**small effective moment**



## “Site Selective Mott transition”,

Hyowon Park, Andrew J. Millis, and Chris A. Marianetti, Phys. Rev. Lett. **109**, 156402 (2012) .

G. Sawatzky, arXiv 1608.01645

Other approaches postulate  $d^8$  and can not justify without experiment.

## The exact double-counting gives Ni $d^8$ configuration.

Haule & Pascut, ScientificReports7(2017)10375.

With two holes in the high-spin state, **Hund’s coupling** induces strong correlations and Mott physics.

# Double-Counting of Hartree

**Exact Hartree:**  $E_{V_C}^H[\rho] = \frac{1}{2} \int d\mathbf{r}d\mathbf{r}' V_C(|\mathbf{r} - \mathbf{r}'|) \rho(\mathbf{r}) \rho(\mathbf{r}')$

**LDA approximation**

Exact Hartree Hartree term included

$$E_{V_C}^H[\rho] = \frac{1}{2} \int d\mathbf{r}d\mathbf{r}' V_C(|\mathbf{r} - \mathbf{r}'|) \rho(\mathbf{r}) \rho(\mathbf{r}')$$

**DMFT approximation**

density projected & interaction screened

$\rho \rightarrow \hat{P}\rho$  &  $V_C \rightarrow V_{DMFT}$

$$E_{DMFT}^H[\rho] = \frac{1}{2} \int d\mathbf{r}d\mathbf{r}' (\hat{P}\rho(\mathbf{r})) (\hat{P}\rho(\mathbf{r}')) V_{DMFT}(\mathbf{r} - \mathbf{r}')$$

This approximation for Hartree term appears in  $\Phi^{DMFT}$

Double counting to subtract is the DMFT approximation for the Hartree term:

$$\Phi_{DMFT}^{DC, Hartree}[\{\rho\}] = \frac{1}{2} \int d\mathbf{r}d\mathbf{r}' (\hat{P}\rho(\mathbf{r})) (\hat{P}\rho(\mathbf{r}')) V_{DMFT}(\mathbf{r} - \mathbf{r}')$$

# Double-Counting of Exchange

**Exact Exchange:**

$$E^X[\rho] = -\frac{1}{2} \int d\mathbf{r}d\mathbf{r}' \rho(\mathbf{r}, \mathbf{r}') \rho(\mathbf{r}', \mathbf{r}) V_C(|\mathbf{r} - \mathbf{r}'|)$$

**LDA approximation:**

exchange of electron gas,  
matching electron density

$$E_F = (2\pi^2 \rho)^{2/3} / (2m) \text{ and}$$

$$\rho_\sigma^0(\mathbf{r}, \mathbf{r}') = \int \frac{d^3k}{(2\pi)^3} e^{i\mathbf{k}(\mathbf{r}-\mathbf{r}')} f\left(\frac{k^2}{2m} - E_F\right)$$

$$E_{LDA}^X[\rho] = -\frac{1}{2} \int d\mathbf{r}d\mathbf{r}' \rho^0(\mathbf{r}, \mathbf{r}') \rho^0(\mathbf{r}', \mathbf{r}) V_C(|\mathbf{r} - \mathbf{r}'|)$$

$$E_{LDA}^X[\rho] = -\frac{0.9163 \text{ Ry}}{\left(\frac{3}{4\pi} \rho\right)^{1/3}}$$

**DMFT approximation**

density projected &  
interaction screened

$$\rho \rightarrow \hat{P}\rho \text{ \& \ } V_C \rightarrow V_{DMFT}$$

$$E_{V_{DMFT}}^X[\rho] = -\frac{1}{2} \int d\mathbf{r}d\mathbf{r}' (\hat{P}\rho(\mathbf{r}, \mathbf{r}')) (\hat{P}\rho(\mathbf{r}', \mathbf{r})) V_{DMFT}(|\mathbf{r} - \mathbf{r}'|)$$

$$E_{V_{DMFT}}^X[\{\rho\}] = -\frac{1}{2} \int d\mathbf{r}d\mathbf{r}' \left( \sum_{mm'} \langle \mathbf{r} | \phi_m^i \rangle \langle \phi_m^i | \rho | \phi_{m'}^i \rangle \langle \phi_{m'}^i | \mathbf{r}' \rangle \right) \left( \sum_{m''m'''} \langle \mathbf{r}' | \phi_{m''}^i \rangle \langle \phi_{m''}^i | \rho | \phi_{m'''}^i \rangle \langle \phi_{m'''}^i | \mathbf{r} \rangle \right) V_{DMFT}(\mathbf{r} - \mathbf{r}')$$

$$= -\frac{1}{2} \sum_{m,m',m'',m'''} \langle \phi_m^i | \rho | \phi_{m'}^i \rangle \langle \phi_{m''}^i | \rho | \phi_{m'''}^i \rangle \int d\mathbf{r}d\mathbf{r}' \phi_{m'''}^{i*}(\mathbf{r}) \phi_{m'}^{i*}(\mathbf{r}') V_{DMFT}(\mathbf{r} - \mathbf{r}') \phi_{m''}^i(\mathbf{r}') \phi_m^i(\mathbf{r})$$

$$= -\frac{1}{2} \sum_{m,m',m'',m'''} \rho_{mm'}^i \rho_{m''m'''}^i \langle \phi_{m'''}^i \phi_{m'}^i | V_{DMFT} | \phi_{m''}^i \phi_m^i \rangle$$

# Double-Counting of Exchange

**Exact Exchange:**

$$E^X[\rho] = -\frac{1}{2} \int d\mathbf{r}d\mathbf{r}' \rho(\mathbf{r}, \mathbf{r}') \rho(\mathbf{r}', \mathbf{r}) V_C(|\mathbf{r} - \mathbf{r}'|)$$

**LDA approximation:**

exchange of electron gas,  
matching electron density

$$E_F = (2\pi^2 \rho)^{2/3} / (2m) \text{ and}$$

$$\rho_\sigma^0(\mathbf{r}, \mathbf{r}') = \int \frac{d^3k}{(2\pi)^3} e^{i\mathbf{k}(\mathbf{r}-\mathbf{r}')} f\left(\frac{k^2}{2m} - E_F\right)$$

$$E_{LDA}^X[\rho] = -\frac{1}{2} \int d\mathbf{r}d\mathbf{r}' \rho^0(\mathbf{r}, \mathbf{r}') \rho^0(\mathbf{r}', \mathbf{r}) V_C(|\mathbf{r} - \mathbf{r}'|)$$

**DMFT approximation**

density projected &  
interaction screened

$$\rho \rightarrow \hat{P}\rho \text{ \& } V_C \rightarrow V_{DMFT}$$

$$E_{V_{DMFT}}^X[\rho] = -\frac{1}{2} \int d\mathbf{r}d\mathbf{r}' (\hat{P}\rho(\mathbf{r}, \mathbf{r}')) (\hat{P}\rho(\mathbf{r}', \mathbf{r})) V_{DMFT}(|\mathbf{r} - \mathbf{r}'|)$$

Intersection of both approximations: apply **both approximations** to the functional

- 1) Interaction is screened in DC term
- 2) Use projected density in DC term
- 3) Replace exact expression by electron gas expression

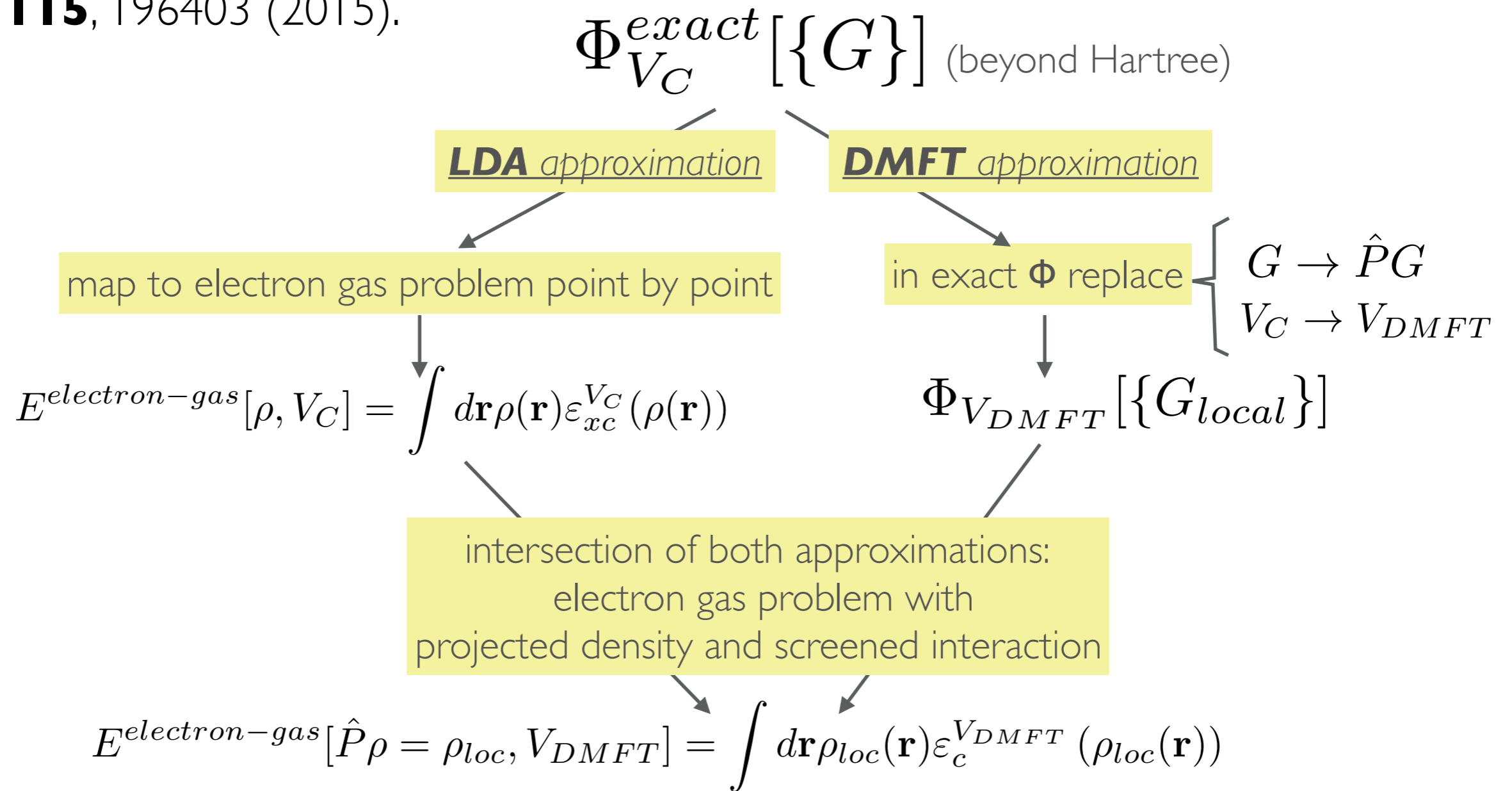
Result is:  $\Phi^{DC,X} = -\frac{1}{2} \int d\mathbf{r}d\mathbf{r}' \rho^0(\mathbf{r}, \mathbf{r}') \rho^0(\mathbf{r}', \mathbf{r}) V_{DMFT}(\mathbf{r} - \mathbf{r}')$

$$\rho^0(\mathbf{r}, \mathbf{r}') = \int \frac{d^3k}{(2\pi)^3} e^{i\mathbf{k}(\mathbf{r}-\mathbf{r}')} f\left(\frac{k^2}{2m} - E_F\right) \quad E_F = \left(2\pi^2 (\hat{P}\rho)^{2/3}\right) / (2m)$$



# Double-Counting of Correlations

KH, PRL **115**, 196403 (2015).

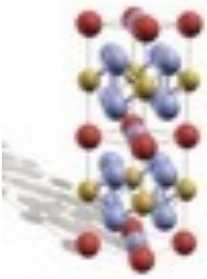


Double counting:

$$\Phi^{DC}[\rho_{local}] = \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \rho_{local}(\mathbf{r}) V_{DMFT}(\mathbf{r} - \mathbf{r}') \rho_{local}(\mathbf{r}') + \int d\mathbf{r} \rho_{local}(\mathbf{r}) \epsilon_{xc}^{V_{DMFT}}[\rho_{local}(\mathbf{r})]$$

electron gas interacting with screened Coulomb interaction

# Summary for Double-Counting



EDMFTF Functional:

$$\Gamma[G] = \text{Tr} \log G - \text{Tr}((G_0^{-1} - G^{-1})G) + E_{Vc}^{H+XC}[\rho] + \Phi_{V_{DMFT}}^{DMFT}[G_{local}] - \Phi_{V_{DMFT}}^{H+XC}[\rho_{local}]$$

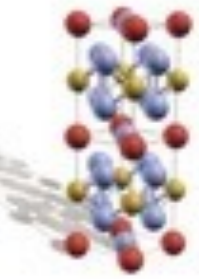
Double-counting functional:

*DMFT approximation on LDA functional OR LDA approximation on DMFT functional :*

$$\Phi_{V_{DMFT}}^{H+XC}[\rho_{local}] = \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \rho_{local}(\mathbf{r}) V_{DMFT}(\mathbf{r} - \mathbf{r}') \rho_{local}(\mathbf{r}') + \int d\mathbf{r} \rho_{local}(\mathbf{r}) \epsilon_{xc}^{V_{DMFT}}[\rho_{local}(\mathbf{r})]$$

electron gas interacting with screened Coulomb interaction!  
only the DMFT charge density enters.

# Embedded Dynamical Mean Field Theory Functional



Stationary **Embedded DMFT** functional extremized in real space.



Free energy functional can be **analytically differentiated to give forces on all atoms.**

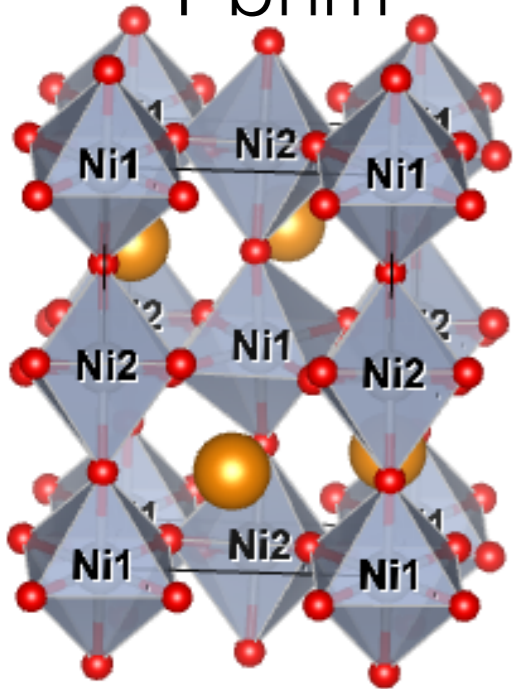


Can predict complex crystal structures

see : Phys. Rev. B **94**, 195146 (2016).

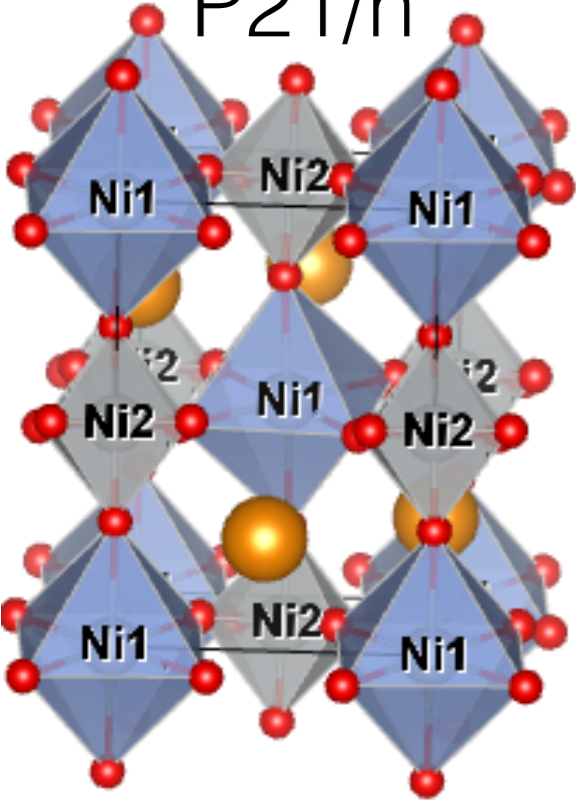
# Optimized Structure NdNiO<sub>3</sub>

Pbnm



Pbnm	Exp.	EDMFTF-PARA		GGA
Ni	(0.000, 0.000, 0.500)	(0.000, 0.000, 0.500)		(0.000, 0.000, 0.500)
O <sub>1</sub>	(0.216, 0.287, 0.539)	(0.214, 0.287, 0.539)		(0.207, 0.294, 0.547)
O <sub>2</sub>	(0.569, 0.490, 0.750)	(0.573, 0.490, 0.750)		(0.591, 0.477, 0.750)
Nd	(0.496, 0.035, 0.750)	(0.491, 0.044, 0.750)		(0.488, 0.058, 0.750)
$\sqrt{\langle(\mathbf{r} - \mathbf{r}_{exp})^2\rangle}$		0.0056		0.0190
P21/n	Exp	EDMFTF-PARA	EDMFT-AFM	GGA+U
Ni <sub>1</sub>	(0.000, 0.000, 0.000)	(0.000, 0.000, 0.000)	(0.000, 0.000, 0.000)	(0.000, 0.000, 0.000)
Ni <sub>2</sub>	(0.000, 0.000, 0.500)	(0.000, 0.000, 0.500)	(0.000, 0.000, 0.500)	(0.000, 0.000, 0.500)
O <sub>1</sub>	(0.575, 0.487, 0.752)	(0.575, 0.489, 0.754)	(0.574, 0.489, 0.750)	(0.595, 0.475, 0.755)
O <sub>2</sub>	(0.214, 0.276, 0.527)	(0.209, 0.284, 0.540)	(0.209, 0.285, 0.540)	(0.198, 0.291, 0.549)
O <sub>3</sub>	(0.719, 0.204, 0.447)	(0.717, 0.209, 0.460)	(0.717, 0.210, 0.460)	(0.711, 0.198, 0.452)
Nd	(0.493, 0.039, 0.750)	(0.491, 0.044, 0.750)	(0.493, 0.044, 0.750)	(0.489, 0.056, 0.750)
$\sqrt{\langle(\mathbf{r} - \mathbf{r}_{exp})^2\rangle}$		0.0090	0.0091	0.0180

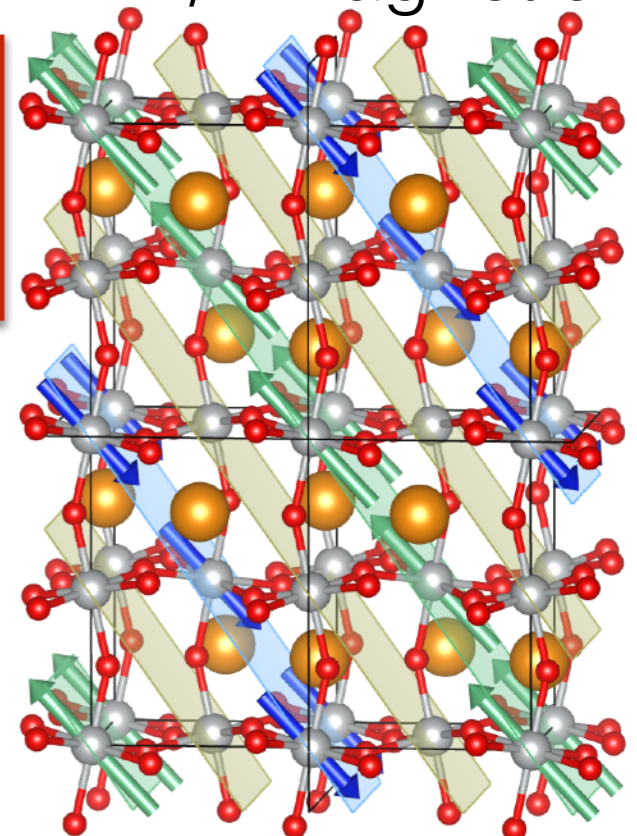
P21/n



With the single functional we optimize all three structures.

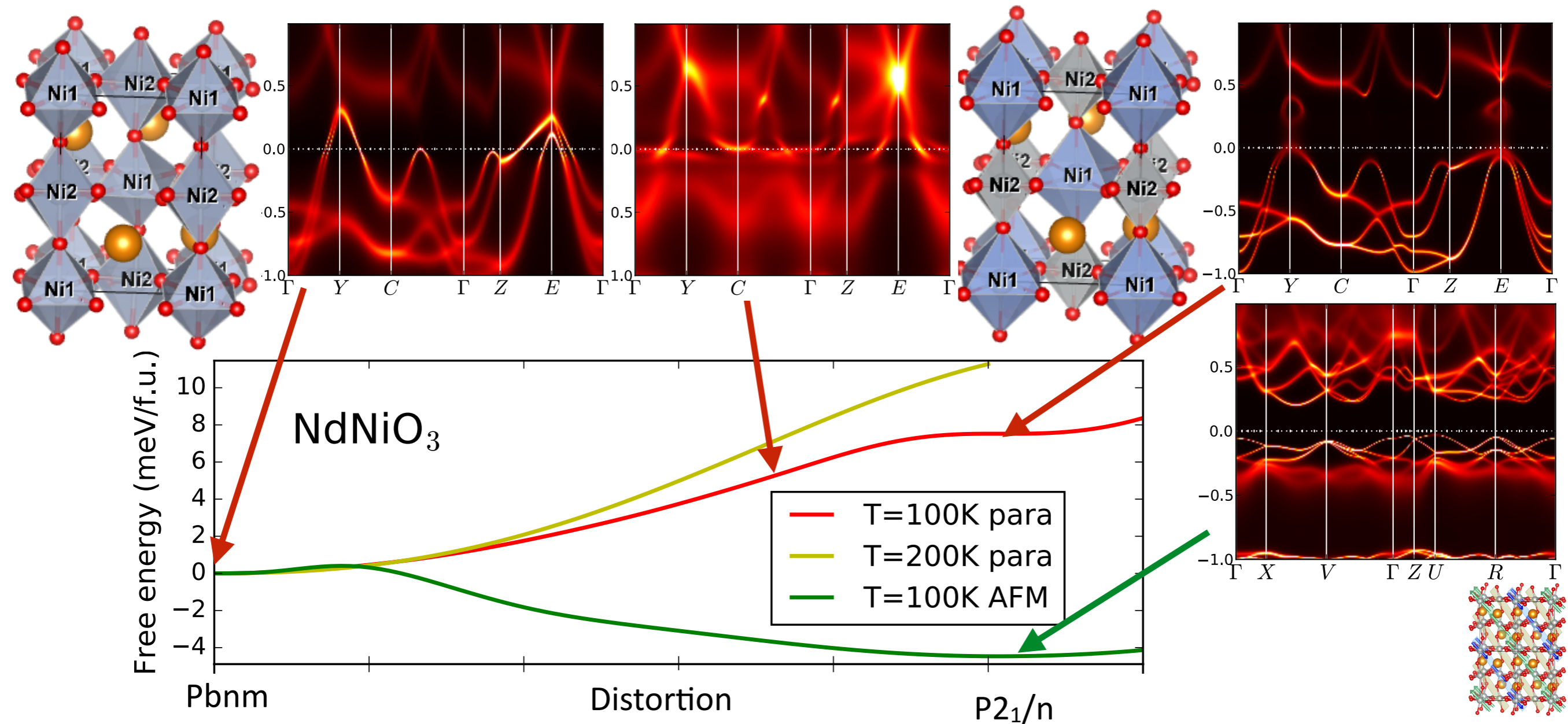
Agreement with experiment 2-3 times better than the best of GGA or GGA+U.

P21/n magnetic

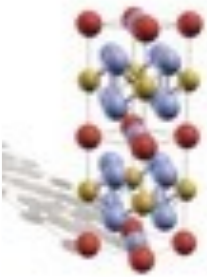


# Energetic of the Mott transition in NdNiO<sub>3</sub>

- Paramagnetic Mott insulating state exists in NdNiO<sub>3</sub> (we optimized it), but is metastable
- Magnetism stabilizes the insulating state, but is not driving the MIT. Fluctuating moments release their entropy by ordering and system gains some energy.



# Force on all atoms from derivative of the functional



$$\frac{\delta\Gamma[G]}{\delta\mathbf{R}_\mu} = \frac{\delta G}{\delta\mathbf{R}_\mu} \left( \frac{\partial\Gamma[G]}{\partial G} \right)_{R_\mu} + \left( \frac{\partial\Gamma[G]}{\partial\mathbf{R}_\mu} \right)_G$$

vanishes

$$\begin{aligned} \frac{\delta\Gamma[\{G\}]}{\delta\mathbf{R}_\mu} &= \frac{\partial}{\partial\mathbf{R}_\mu} (\text{Tr} \log(G) - \text{Tr}((G_0^{-1} - G^{-1})G) + \Phi[\{G\}] + E_{nuc-nuc})_G \\ &= \frac{\partial}{\partial\mathbf{R}_\mu} (-\text{Tr}([i\omega + \mu + \nabla^2 - V_{nuc}(\mathbf{r})]\delta(\mathbf{r} - \mathbf{r}')G) + E_{nuc-nuc}) \\ &= \text{Tr}(\rho \frac{\partial}{\partial\mathbf{R}_\mu} V_{nuc}) + \frac{\partial}{\partial\mathbf{R}_\mu} E_{nuc} \end{aligned}$$

$$\mathbf{F}^{HF} = -\text{Tr}(\rho \frac{\partial V_{nuc}}{\partial\mathbf{R}_\mu}) - \frac{\partial E_{nuc}}{\partial\mathbf{R}_\mu}$$

The Hellman-Feynman force

# Force on all atoms from derivative of the functional

---

The DMFT projector is not fixed in space, but rather moves with the atom, and the LAPW basis set also moves with the atoms.

→ **“Pulay forces”** appear

**We need to differentiate the implemented expression for the free energy.**

# Free energy expression again

Recall:

$$\Gamma[\{G\}] = \text{Tr} \log G - \text{Tr}((G_0^{-1} - G^{-1})G) + E_{V_C}^{H+XC}[\rho] + \sum_{\mathbf{R}_i \in \text{corr}} \Phi_{V_{DMFT}}^{DMFT}[G_{loc}^i] - \Phi_{V_{DMFT}}^{DC}[\rho_{loc}^i]$$

at the DMFT solution the Dyson Eq. is satisfied

$$G^{-1} = G_0^{-1} - V_{H+XC}(\mathbf{r})\delta(\mathbf{r} - \mathbf{r}')\delta(\tau - \tau') - \langle \mathbf{r} | \phi_\alpha^i \rangle (\Sigma^{imp} - V^{DC})_{\alpha\beta} \langle \phi_\beta^i | \mathbf{r}' \rangle$$

hence the free can be computed by

$$F = \text{Tr} \log(G) - \text{Tr}(V_{H+XC})\rho + E^{H+XC}[\rho] + \sum_{\mathbf{R}_i} \left\{ -\text{Tr}((\Sigma^{imp} - V^{DC})G_{loc}^i) + \Phi^{DMFT}[G_{loc}^i] - \Phi^{DC}[\rho_{loc}^i] \right\}$$

nuclear-nuclear energy is added;  
canonical ensemble needs  $+\mu N$



# Free energy expression implementation

---

To implement  $\text{Tr} \log G$  we compute generalized Kohn-Sham orbitals:

$$\langle \psi_{j\mathbf{k}\omega_n} | \left( T + V_{nuc} + V_{H+XC} + \sum_{mm', \mathbf{R}_\mu} |\phi_m^\mu\rangle \langle \phi_m^\mu| \Sigma_{i\omega_n} - V_{DC} |\phi_{m'}^\mu\rangle \langle \phi_{m'}^\mu| \right) | \psi_{i\mathbf{k}\omega_n} \rangle = \delta_{ij} \varepsilon_{\mathbf{k}\omega_n, i}$$

so that  $\langle \psi_{j\mathbf{k}\omega_n} | G | \psi_{i\mathbf{k}\omega_n} \rangle = \frac{\delta_{ij}}{i\omega_n + \mu - \varepsilon_{\mathbf{k}\omega_n, i}}$ , i.e.,  $G$  is diagonalized

then

$$\text{Tr} \log(-G) = -\text{Tr} \log(-i\omega_n - \mu + \varepsilon_{\mathbf{k}\omega_n})$$

and

$$F = -\text{Tr} \log(-i\omega_n - \mu + \varepsilon_{\mathbf{k}\omega_n}) - \text{Tr}(V_{H+XC})\rho + E^{H+XC}[\rho] + E_{nuc-nuc} + \mu N + \sum_{\mathbf{R}_i} \left\{ -\text{Tr}((\Sigma - V_{DC})G_{loc}^i) + \Phi^{DMFT}[G_{loc}^i] - \Phi^{DC}[\rho_{loc}^i] \right\}$$

# Derivative of the free energy

The free energy :

$$F = \underbrace{-\text{Tr} \log(-i\omega_n - \mu + \varepsilon_{\mathbf{k}\omega_n})}_{\text{Term 1}} - \underbrace{\text{Tr}(V_{H+XC})\rho}_{\text{Term 2}} + \underbrace{E^{H+XC}[\rho]}_{\text{Term 3}} + \underbrace{E_{nuc-nuc}}_{\text{Term 4}} + \underbrace{\mu N}_{\text{Term 5}} + \sum_{\mathbf{R}_i} \left\{ \underbrace{-\text{Tr}((\Sigma - V_{DC})G_{loc}^i)}_{\text{Term 6}} + \underbrace{\Phi^{DMFT}[G_{loc}^i]}_{\text{Term 7}} - \underbrace{\Phi^{DC}[\rho_{loc}^i]}_{\text{Term 8}} \right\}$$

$$\frac{\delta F}{\delta \mathbf{R}_\mu} = \text{Tr} \left( \frac{1}{i\omega + \mu - \varepsilon_{\mathbf{k}\omega_n}} \frac{\delta(\varepsilon_{\mathbf{k}\omega_n} - \mu)}{\delta \mathbf{R}_\mu} \right) - \text{Tr} \left( \rho \frac{\delta V_{H+XC}}{\delta \mathbf{R}_\mu} \right) + \frac{\delta E_{nuc-nuc}}{\delta \mathbf{R}_\mu} + N \frac{\delta \mu}{\delta \mathbf{R}_\mu} - \text{Tr} \left( G_{loc} \frac{\delta \Sigma - \delta V_{DC}}{\delta \mathbf{R}_\mu} \right)$$

$$\frac{\delta F}{\delta \mathbf{R}_\mu} = \text{Tr} \left( \frac{1}{i\omega + \mu - \varepsilon_{\mathbf{k}\omega_n}} \frac{\delta(\varepsilon_{\mathbf{k}\omega_n})}{\delta \mathbf{R}_\mu} \right) - \text{Tr} \left( \rho \frac{\delta(V_{KS})}{\delta \mathbf{R}_\mu} \right) - \text{Tr} \left( G_{loc} \frac{\delta \Sigma - \delta V_{DC}}{\delta \mathbf{R}_\mu} \right)$$

Recall:  $\mathbf{F}^{HF} = -\text{Tr} \left( \rho \frac{\partial V_{nuc}}{\partial \mathbf{R}_\mu} \right) - \frac{\partial E_{nuc}}{\partial \mathbf{R}_\mu}$

# Derivative of the free energy

$$\mathbf{F}_\mu^{Puly} = -\text{Tr} \left( \frac{1}{i\omega_n + \mu - \varepsilon_{\mathbf{k}\omega_n}} \frac{\delta \varepsilon_{\mathbf{k}\omega_n}}{d\mathbf{R}_\mu} \right) + \text{Tr} \left( \rho \frac{\delta V_{KS}}{\delta \mathbf{R}_\mu} \right) + \text{Tr} \left( G_{loc} \frac{\delta \Sigma - \delta V_{DC}}{\delta \mathbf{R}_\mu} \right)$$

$\delta \Sigma(\omega)$  very hard to compute.

appears in two terms.

$$\delta \Sigma / \delta G = \delta^2 \Phi / \delta G^2$$

*But: Functional is stationary, and  $\delta \Sigma(\omega)$  cancel out.*

# Derivative of the free energy

To prove that  $\delta(\Sigma - V_{DC})$  cancels, we recall eigenvalue Eq.

$$\langle \psi_{i\mathbf{k}\omega_n} | \left( T + V_{nuc} + V_{H+XC} + \sum_{mm', \mathbf{R}_\mu} |\phi_m^\mu\rangle \langle \phi_m^\mu| \Sigma_{i\omega_n} - V_{DC} |\phi_{m'}^\mu\rangle \langle \phi_{m'}^\mu| \right) - \varepsilon_{\mathbf{k}\omega_n, i} | \psi_{i\mathbf{k}\omega_n} \rangle = 0$$

which is satisfied for each atomic position  $\mathbf{R}_\mu$  hence

$$\langle \psi_{i\mathbf{k}\omega_n} | \left( \delta(T + V_{nuc} + V_{H+XC}) + \sum_{mm', \mathbf{R}_\mu} \delta(|\phi_m^\mu\rangle \langle \phi_m^\mu| \Sigma_{i\omega_n} - V_{DC} |\phi_{m'}^\mu\rangle \langle \phi_{m'}^\mu|) \right) - \delta\varepsilon_{\mathbf{k}\omega_n, i} | \psi_{i\mathbf{k}\omega_n} \rangle = 0$$

therefore 
$$\delta\varepsilon_{\mathbf{k}\omega_n, i} = \sum_{\mathbf{R}_\mu, mm'} \langle \psi_{i\mathbf{k}\omega_n} | \phi_m^\mu \rangle \langle \phi_m^\mu | \delta(\Sigma - V_{DC}) | \phi_{m'}^\mu \rangle \langle \phi_{m'}^\mu | \psi_{i\mathbf{k}\omega_n} \rangle + \dots$$
  
 ....+derivative of the projector+DFT terms

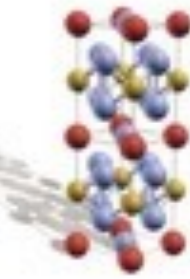
hence

$$\text{Tr} \left( \frac{\delta\varepsilon_{\mathbf{k}\omega_n}}{i\omega + \mu - \varepsilon_{\mathbf{k}\omega_n}} \right) = \text{Tr}(|\psi_{i\mathbf{k}\omega_n}\rangle \frac{1}{i\omega + \mu - \varepsilon_{\mathbf{k}\omega_n}} \langle \psi_{i\mathbf{k}\omega_n}| \sum_{\mathbf{R}_\mu, mm'} |\phi_m^\mu\rangle \langle \phi_m^\mu| \delta(\Sigma - V_{DC}) | \phi_{m'}^\mu\rangle \langle \phi_{m'}^\mu|) + \dots$$

$$= \text{Tr}(G \sum_{\mathbf{R}_\mu, mm'} |\phi_m^\mu\rangle \langle \phi_m^\mu| \delta(\Sigma - V_{DC}) | \phi_{m'}^\mu\rangle \langle \phi_{m'}^\mu|) + \dots$$

$$\mathbf{F}_\mu^{Puly} = -\text{Tr} \left( \frac{1}{i\omega_n + \mu - \varepsilon_{\mathbf{k}\omega_n}} \frac{\delta\varepsilon_{\mathbf{k}\omega_n}}{d\mathbf{R}_\mu} \right) + \text{Tr} \left( \rho \frac{\delta V_{KS}}{\delta \mathbf{R}_\mu} \right) + \text{Tr} \left( G_{loc} \frac{\delta \Sigma - \delta V_{DC}}{\delta \mathbf{R}_\mu} \right) = \text{Tr}(G_{loc} \delta(\Sigma - V_{DC})) + \dots$$

# Final results for forces in a mixed basis set



Pulay force in mixed basis:

DFT-like terms

$$\mathbf{F}_\mu^{Pulay} = -\text{Tr} \left( \tilde{\rho} A^{0\dagger} \frac{\delta H^0}{\delta \mathbf{R}_\mu} A^0 - \widetilde{(\rho\varepsilon)} A^{0\dagger} \frac{\delta O}{\delta \mathbf{R}_\mu} A^0 \right) + \text{Tr} \left( \rho \frac{\delta V_{KS}}{\delta \mathbf{R}_\mu} \right)$$

$$-\frac{1}{\beta} \sum_{i\omega_n} \sum_{\mathbf{K}\mathbf{K}', m'm} \bar{G}_{\mathbf{K}\mathbf{K}'} (\Sigma - V_{DC})_{m'm} \frac{\delta (\langle \chi_{\mathbf{K}'} | \phi_{m'} \rangle \langle \phi_m | \chi_{\mathbf{K}} \rangle)}{\delta \mathbf{R}_\mu}$$

derivative of the DMFT projector, because the DMF basis moves with the atom

depends on the “non-trivial” DMFT density matrices

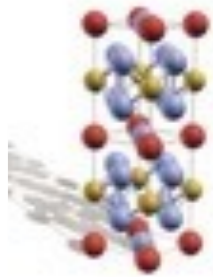
$$\tilde{\rho} \equiv \frac{1}{\beta} \sum_{i\omega_n} B_{\omega_n}^R \frac{1}{i\omega_n + \mu - \varepsilon_{\mathbf{k}\omega_n}} B_{\omega_n}^L$$

$$\widetilde{(\rho\varepsilon)} \equiv \frac{1}{\beta} \sum_{i\omega_n} B_{\omega_n}^R \frac{\varepsilon_{\mathbf{k}\omega_n}}{i\omega_n + \mu - \varepsilon_{\mathbf{k}\omega_n}} B_{\omega_n}^L$$

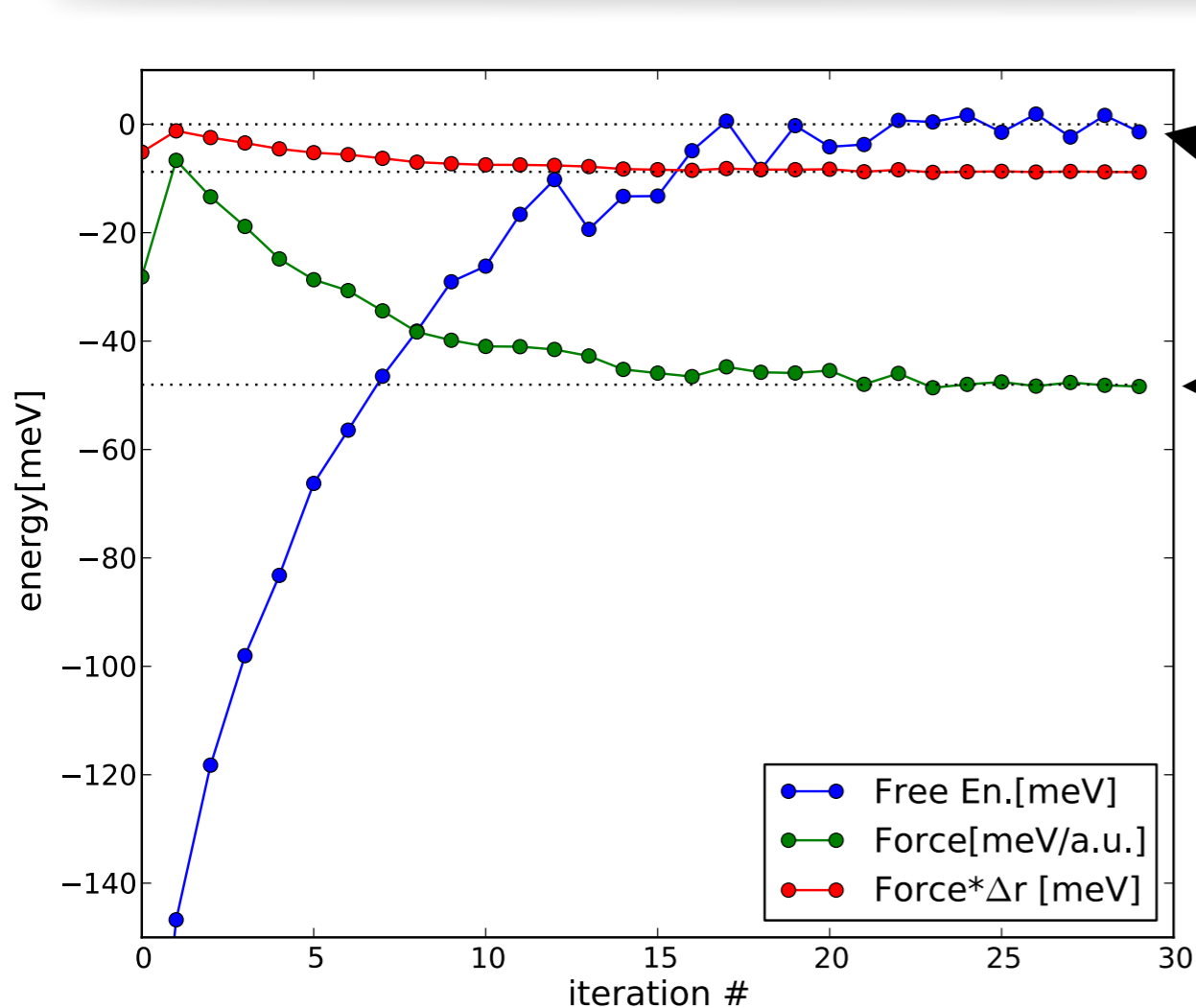
**Success:** Forces do not depend on  $\Phi[G]$  or  $\delta\Sigma/\delta G = \delta^2\Phi/\delta G^2$

which are hard to compute.

K.H. & G.L. Pascut, **Phys. Rev. B** 49, 195146 (2016)



# Forces more stable than free energies



MC noise at constant statistics

free energy noise  $\sim 1$  meV

force noise  $\sim 0.2$  meV/a.u.

Forces very stable!

$$\Phi[G]$$

hard to compute  
(needed for free energy)

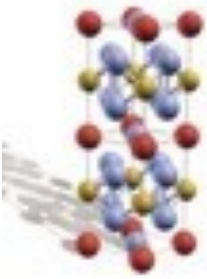
$$\Sigma = \delta\Phi[G]/\delta G$$

easy to compute  
only this is needed for the force

$$\delta^2\Phi[G]/\delta G^2$$

hard to compute  
(needed for dynamical matrix)

# Electronic structure package: eDMFTF



Can be downloaded: <http://hauleweb.rutgers.edu/tutorials>  
tutorials available

- Projection & Embedding instead of downloading in the full potential (APW+lo, LAPW) basis.
- Continuous time quantum Monte Carlo, OCA, NCA...
- Stationary implementation of free energy
- Forces on all atoms
- Structural optimization within DFT+DMFT

**RUTGERS**  
School of Arts and Sciences

Center for Computational  
Materials Theory

## DFT + Embedded DMFT Functional\*

Developed by Kristjan Haule at Rutgers University, ©Copyright 2007-2016.

- [What is DFT+Embedded DMFT Functional](#)
- [Installation](#)
- [Overview](#)
- [Tutorial on single band Hubbard model](#)
- [Tutorial 1 on MnO](#)
- [Tutorial 2 on FeSe, structural optimization, and spectral function plot](#)
- [Tutorial 3 on SrVO<sub>3</sub>](#)
- [Tutorial 4 on LaVO<sub>3</sub>](#)
- [Tutorial 5 on elemental Cerium](#)
- [Tutorial 6 on Sr<sub>2</sub>IrO<sub>4</sub>](#)
- [FAQ](#)

Database:

<http://hauleweb.rutgers.edu/>

**Rutgers DFT & DMFT Material Database**  
Supported by NSF CAREER DMR-0746395 (Kristjan Haule)  
& NSF DMR-0906943 (Gabriel Kotliar)

Home Tutorials Introduction LMTO Database W2K Database W2K Documentation Downloads

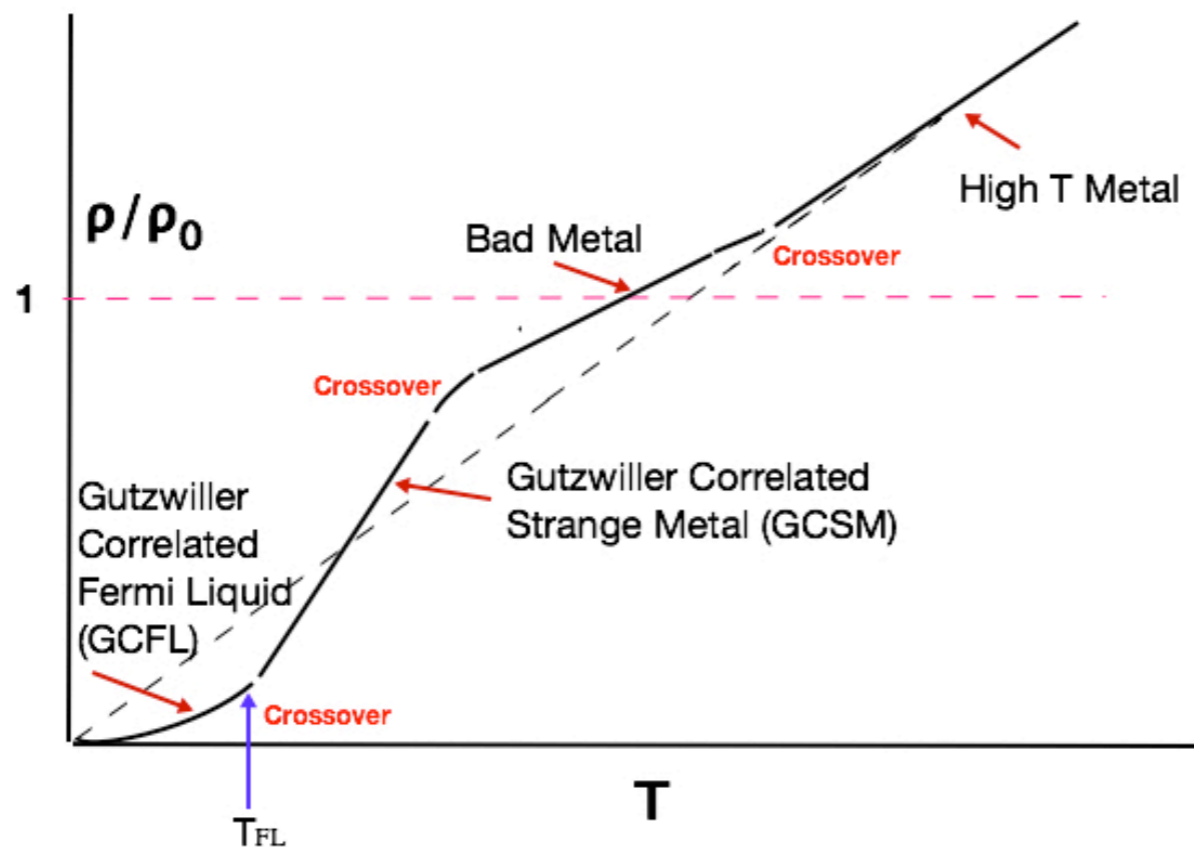
Download the DMFT-Wien2K source code

[dmft\\_w2k.tgz \(version 2012\)](#)

[dmft\\_w2k.tgz \(version 2015\)](#)

Thank you!





Generic sketch of DMFT resistivity for the Hubbard-type model:  $\rho_0$  is the Ioffe-Regel limit,  $T_{FL}$  can be vanishingly small close to the MIT, different scales are very model dependent.