DYNAMICAL MEAN FIELD THEORY
+
DENSITY FUNCTIONAL THEORY
FROM FUNCTIONAL PERSPECTIVE

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Support:

NSF

ALFRED P. SLOAN FOUNDATION 1934

ACS Chemistry for Life™

Blavatnik Awards Young Scientists

WHY IS THIS SO HARD TO SOLVE?

Basic laws of Quantum Mechanics were developed in early 1900 (Schroedinger Eq. 1925, Dirac Eq. 1928).

Dirac (1929)

"The underlying physical laws necessary for a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble."

[Proc. Roy. Soc. (London) A123, 714]

Emergence!

We know the Hamiltonian:

$$H = -\sum_i \frac{\nabla_i^2}{2m_e} + \sum_i V_{ext}(\mathbf{r}_i) + \frac{1}{2}\sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}$$

We know the equation:

$$H\Psi(\mathbf{r}, t) = -\partial_t \Psi(\mathbf{r}, t)$$

So....

DIRECT APPROACH TO SCH. EQ.

Perturbation theory does not work:

Kinetic energy: $E_{kin} \approx \frac{1}{2m_e a^2} \approx 0.2\,eV$

Potential energy: $E_{pot} \approx \frac{e^2}{\varepsilon a} \approx 0.5\,eV$

Interaction is non-perturbative.

Direct Numerical approach hopeless:

10^{23} interacting fermions and wave function is fully antisymmetric with respect to electron coordinates and spins

$$\Psi(\mathbf{r}_1\sigma_1, \mathbf{r}_2\sigma_2, \cdots, \mathbf{r}_N\sigma_N)$$

Sign problem NP hard => cost scales: Exp(-size/T)

INDIRECT APPROACH / STANDARD THEORY

Density Functional Theory:

Hohengerb & Kohn proved: ∃functional of electron density **ρ**, which is minimized at the physical density, and gives ground state energy.

$$E[\{\rho(\mathbf{r})\}] = \underbrace{E_{kin}[\{\rho\}] + E_{int}[\{\rho\}]}_{\text{universal functional}} + \int d\mathbf{r} V_{ext}(\mathbf{r})\rho(\mathbf{r})$$

universal functional: independent of material, depends on EM interaction

material dependent term

Kohn & Sham (1965): To minimize the functional:
solve auxiliary single-particle problem+self-consistency condition

$$\left(\frac{-\hbar^2}{2m_e}\nabla^2 + V_{ext}(\mathbf{r}) + V_{Hartree}(\mathbf{r})\right)\psi_n(\mathbf{r}) + V_{XC}[\{\rho(\mathbf{r})\}]\psi_n(\mathbf{r}) = \varepsilon_n\psi_n(\mathbf{r})$$

self-consistency condition:

$$\rho(\mathbf{r}) = \sum_{\varepsilon_n<\mu} \psi_n^*(\mathbf{r})\psi_n(\mathbf{r})$$

auxiliary potential:

$$V_{XC}[\{\rho(\mathbf{r})\}]$$

unknown but universal

LOCAL DENSITY APPROXIMATION

Universal but unknown functional

$$E_{int}[\{\rho(\mathbf{r})\}] = E_{Hartree}[\{\rho(\mathbf{r})\}] + E_{XC}[\{\rho(\mathbf{r})\}]$$

approximated by local ansatz:

$$E_{XC}[\{\rho(\mathbf{r})\}] \approx \int d\mathbf{r}\rho(\mathbf{r})\varepsilon_{xc}(\rho(\mathbf{r}))$$

energy density at point r depends only on the charge density at the same point.

$\varepsilon_{xc}(n)$ computed in uniform electron gas (jellium) model by QMC

DIFFERENT INDIRECT APPROACH
LUTTINGER-WARD FUNCTIONAL

Joaquin M. Luttinger

Luttinger-Ward Functional:

$$\Gamma[\{G\}] = -\mathrm{Tr}((G_0^{-1} - G^{-1})G) + \underbrace{\mathrm{Tr}\log(-G) + \Phi[\{G\}]}$$

material dependent term:
$G_0^{-1}(\mathbf{r},\mathbf{r}') = [\omega + \mu + \nabla^2 - V_{ext}(\mathbf{r})]\delta(\mathbf{r}-\mathbf{r}')$

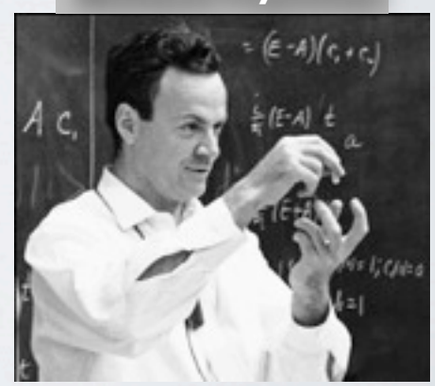
universal functional
independent of material

$\Gamma[G]$ Extremum in the exact Green's function
Γ is free energy in extremum

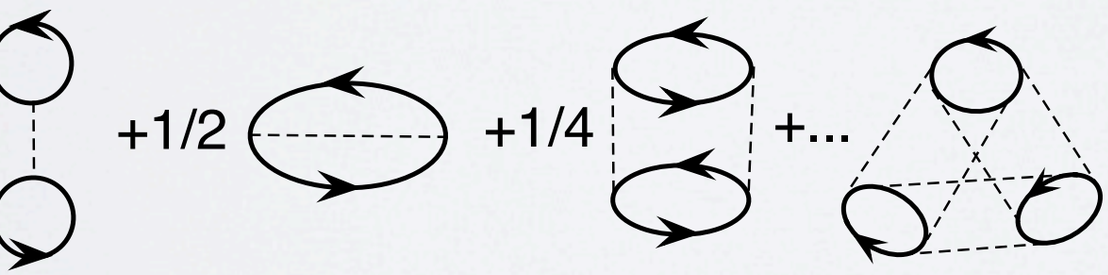
$$\frac{\delta\Gamma[G]}{\delta G} = 0$$

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

Richard Feynman



$\Phi[G] =$ 1/2 +1/2 +1/4 +... +...



legend: G

$v_c(\mathbf{r}-\mathbf{r}') = \frac{1}{|\mathbf{r}-\mathbf{r}'|}$ or U_{ijlk}

For a proof see: Abrikosov, Gorkov, Dzialoszynski book

LW- FUNCTIONAL

$$\Gamma[\{G\}] = -\mathrm{Tr}((G_0^{-1} - G^{-1})G) + \mathrm{Tr}\log(-G) + \Phi[\{G\}]$$

Solution obtained by stationarity

$$\frac{\delta\Gamma[G]}{\delta G} = G^{-1} - G_0^{-1} + \frac{\delta\Phi[G]}{\delta G} = 0$$

$$\frac{\delta\Phi[G]}{\delta G}$$

Functional derivative obtained by cutting G propagator in every diagram in all possible ways

$\Phi[G] =$ 1/2 +1/2 +1/4 +... +...

$\frac{\delta\Phi[G]}{\delta G} =$ + + +... +... $\equiv \Sigma$

G

$v_c(\mathbf{r}-\mathbf{r}') = \frac{1}{|\mathbf{r}-\mathbf{r}'|}$

In practice:
Impossible to solve

USEFUL APPROXIMATIONS

1) Hartree-Fock:

$$\Phi^{HF}[G] =$$ 1/2 +1/2

Stationarity of $\Gamma[G]$ gives: $\Sigma_{HF} =$ +

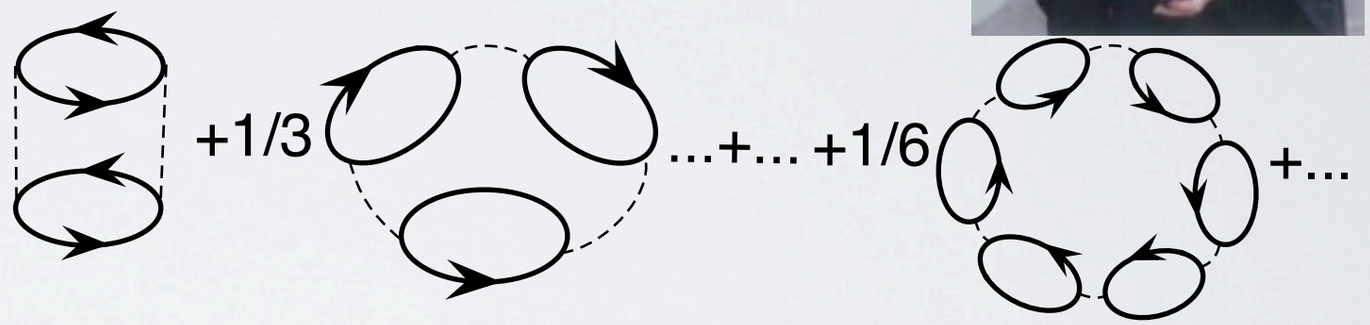
$$\left(\Sigma_{HF} = \frac{\delta \Phi^{HF}[G]}{\delta G}\right)$$

$$\Sigma(\mathbf{r},\mathbf{r}') = \delta(\mathbf{r}-\mathbf{r}') \int d\mathbf{r}'' \rho(\mathbf{r}'',\mathbf{r}'') v_c(\mathbf{r}''-\mathbf{r}) - \rho(\mathbf{r}',\mathbf{r}) v_c(\mathbf{r}'-\mathbf{r})$$

USEFUL APPROXIMATIONS

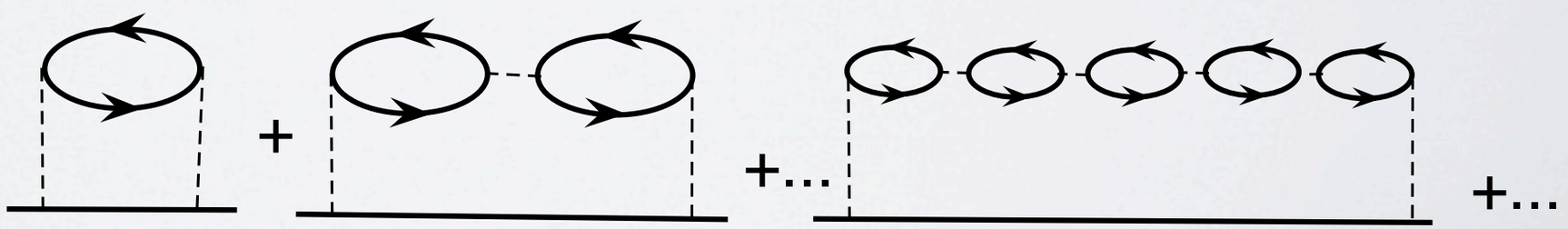
2) RPA (also called GW in abinitio world):

$$\Phi^{GW} = \Phi^{HF}[G] +$$ 1/4 +1/3 ...+... +1/6 +...

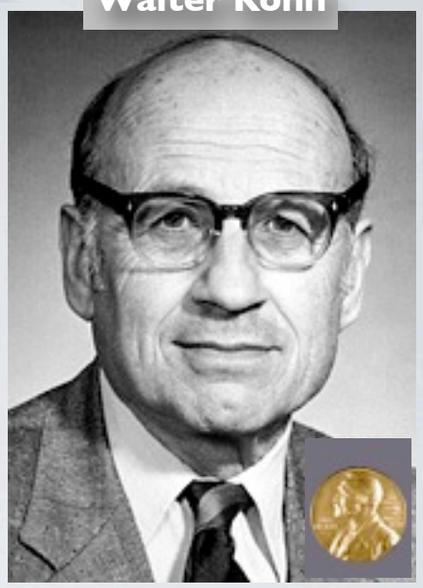


Stationarity of $\Gamma[G]$ gives:

$$\Sigma_{GW} = \Sigma_{HF} +$$ + +... +...



DFT IN LW-LIKE LANGUAGE



electron density $\rho(\mathbf{r}) = G(\mathbf{r}\tau, \mathbf{r}'\tau')\delta(\tau - \tau')\delta(\mathbf{r} - \mathbf{r}')$

is the diagonal part of the GF, i.e.,

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

DFT approximation: $\Phi[\{G\}] \to E_H[\rho] + \Phi_{xc}[\rho]$

While DFT gives exact energy at T=0, in LW language it appears as an approximation to the exact G and F

Consequence for the L.W. like functional:

Stationarity: $G^{-1} - G_0^{-1} = (V_H[\rho] + V_{xc}[\rho])\delta(\tau - \tau')\delta(\mathbf{r} - \mathbf{r}')$

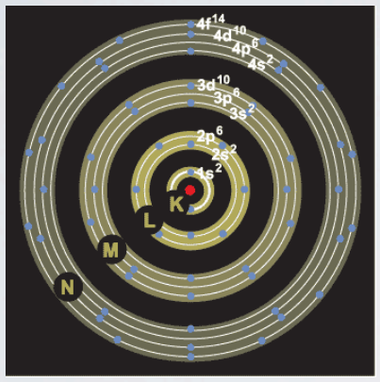
where $G_0^{-1} = -\frac{\partial}{\partial\tau} + \mu + \nabla^2 - V_{ext}$ ← Born-Oppenheimer

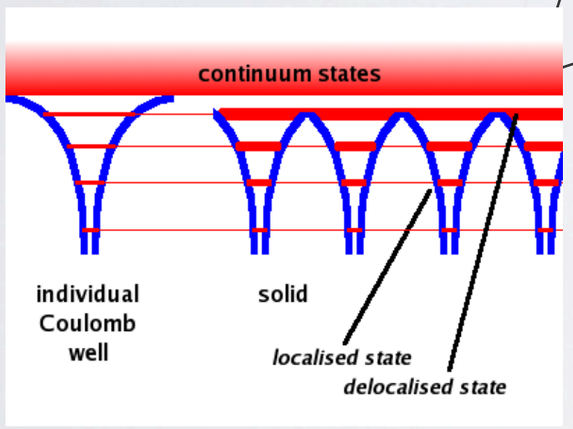
and $\rho(\mathbf{r}) = G(\tau\mathbf{r}, \tau'\mathbf{r}')\delta(\tau - \tau')\delta(\mathbf{r} - \mathbf{r}')$ -- Self-consistency condition

LOCAL/SEMI-LOCAL DENSITY APPR.

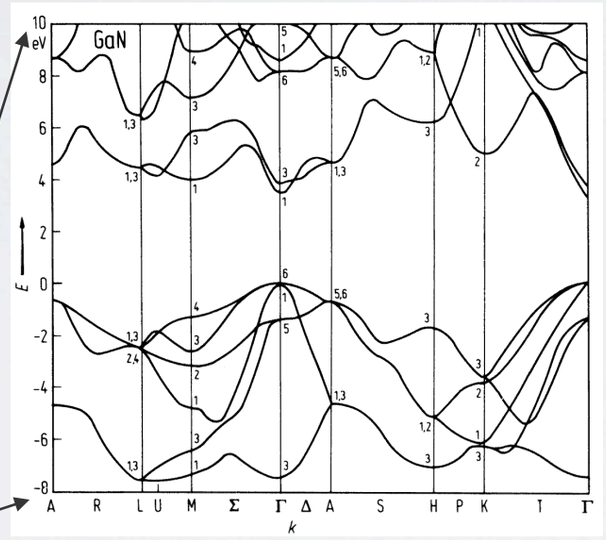
Extraordinary success: Standard theory of the solid state systems

Real space:





Momentum space:

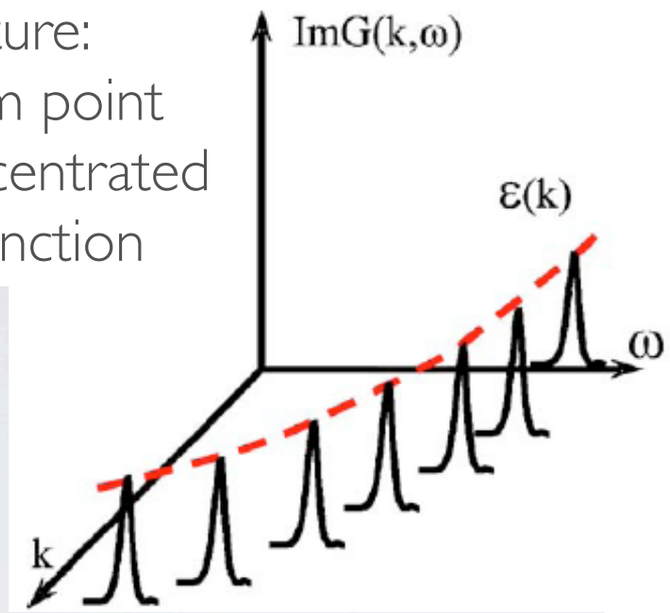


Band Theory: electrons as waves:

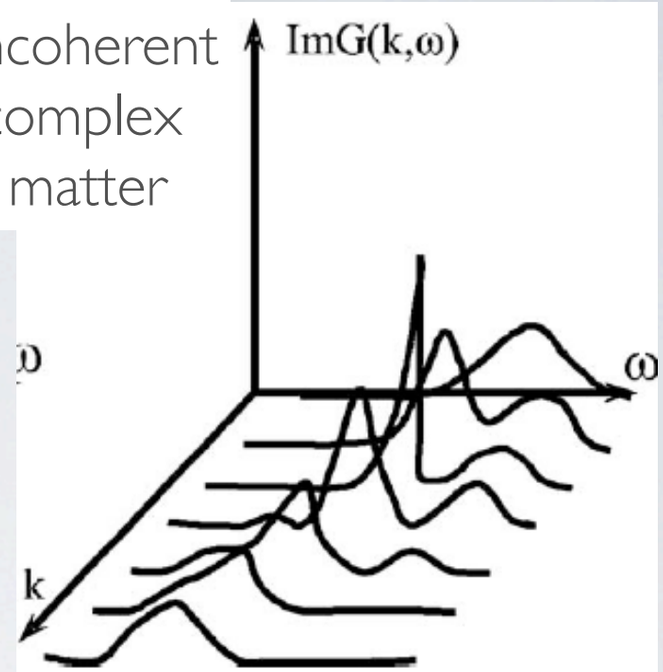
Rigid band picture: En(k) versus k

PROBLEMS IN COMPLEX MAT.

Rigid bands picture:
at each momentum point
electron weight concentrated
in a single delta function

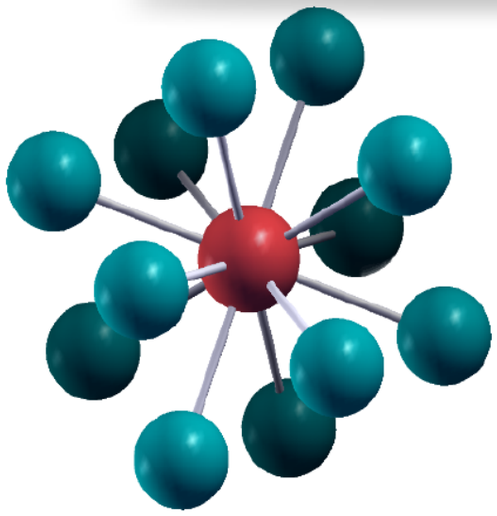


Coherent+incoherent
spectra in complex
correlated matter

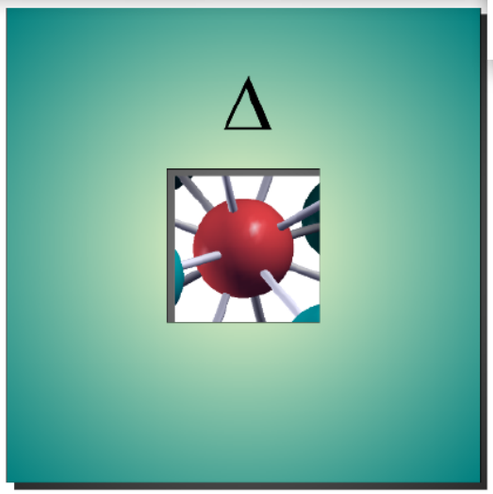


- Electrons have dual nature, partly itinerant and partly localized
- Need to incorporate a real space perspective into wave picture
  (Mot localization -> electrons partly localized,
  Hunds coupling->leads to orbital blocking).

SUCCESSFUL THEORY: DMFT+DFT



solid

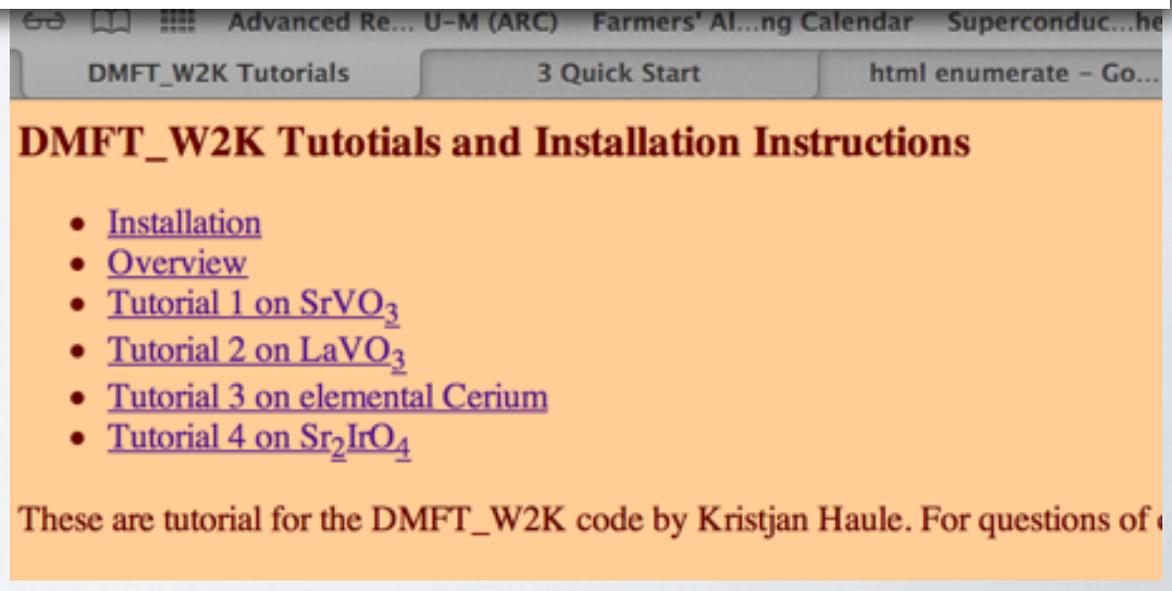


Q. impurity
in a medium

Successfully describes
properties of numerous
complex materials
(see http://hauleweb.rutgers.edu/)

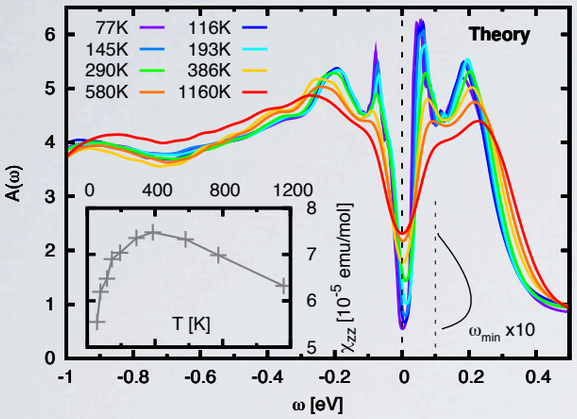
database: http://hauleweb.rutgers.edu

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



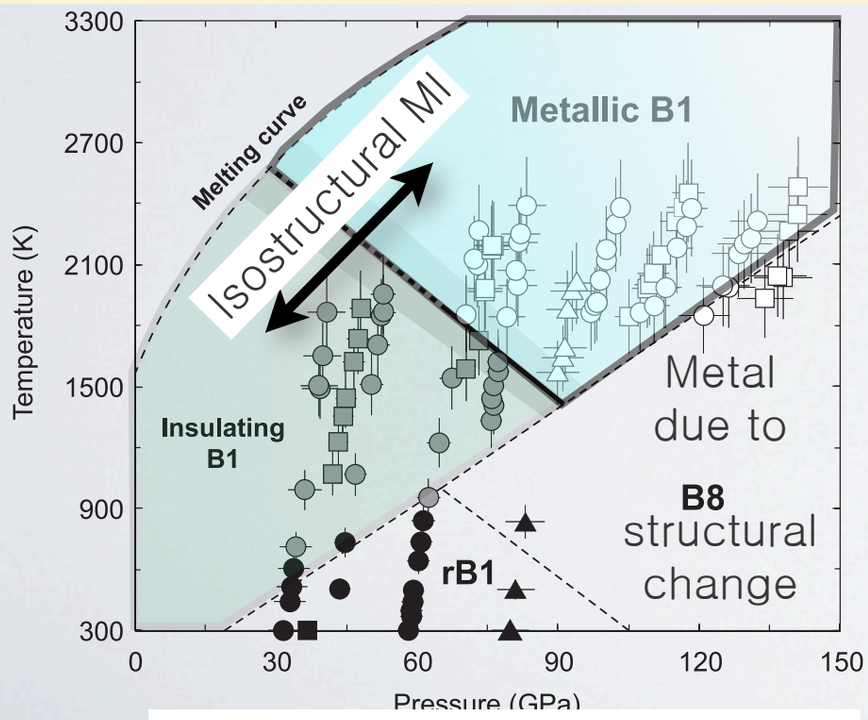
NEW PHYSICS UNCOVERED BY DFT+DMFT

Hund's driven bad semiconducting state in FeSi
Large thermoelectric power



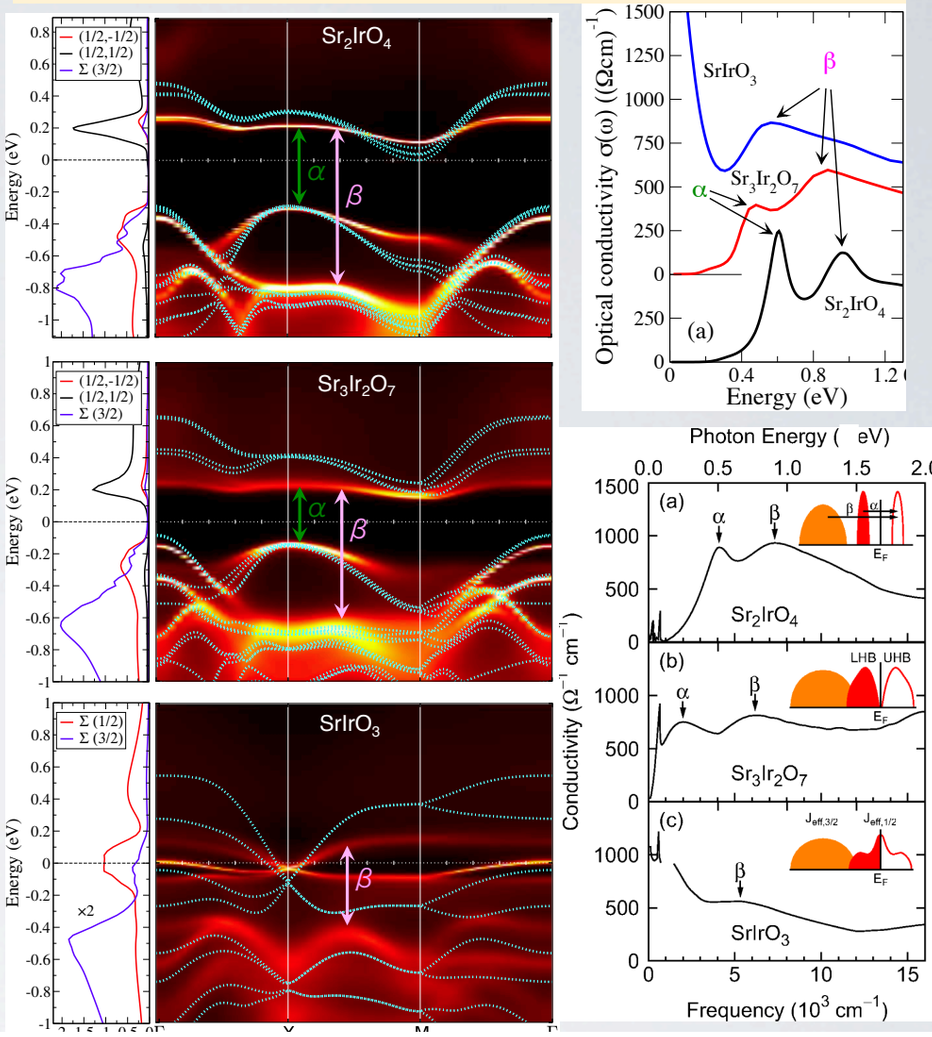
J.M. Tomczak, K. Haule, G. Kotliar, Proceedings of the National Academy of Sciences (2012)

Mott metal insulator transition in FeO at high-T under pressure (**geophysics**)

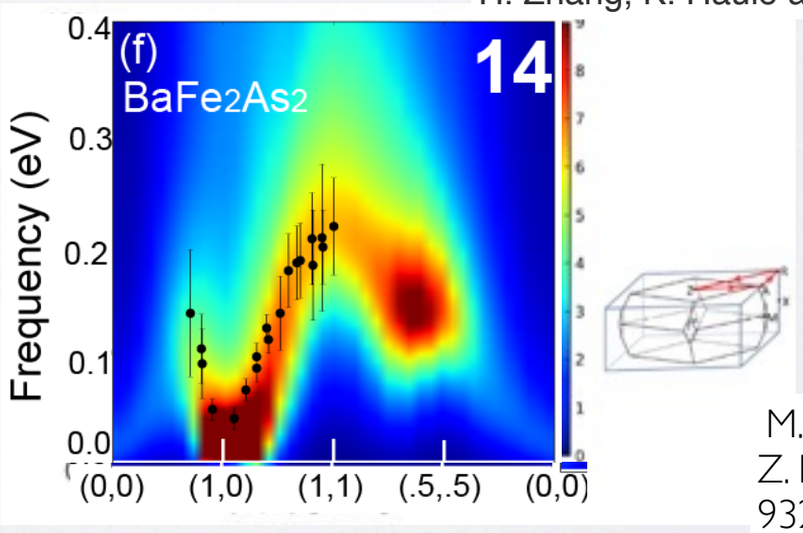


K. Ohta, R.E. Cohen, K. Hirose, K. Haule, K. Shimizu, Y. Ohishi, PRL 2012

Mott transition in RP-Iridates & Jeff=1/2



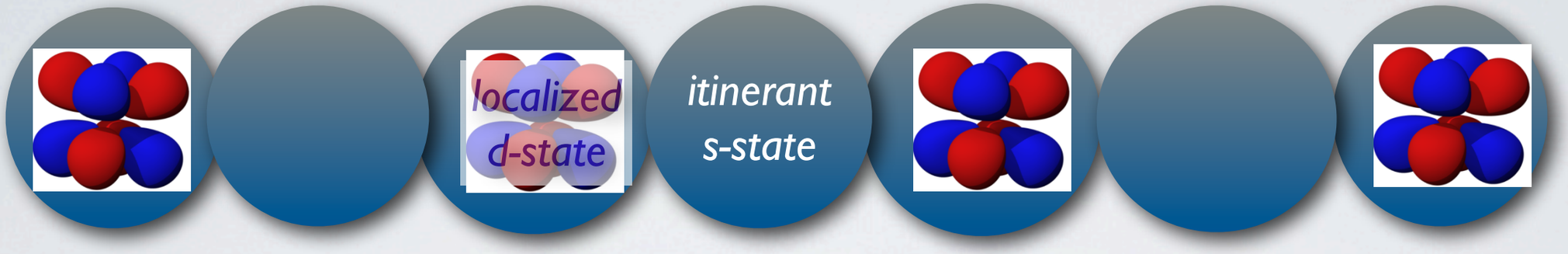
H. Zhang, K. Haule and D. Vanderbilt, PRL 111, 246402 (2013).



Hunds metal physics in iron pnictides and large fluctuating moments

M. Liu, et.al., Nature Physics 8, 376-381 (2012); Z. P. Yin, KH, G. Kotliar, Nature Materials 10, 932-935 (2011)

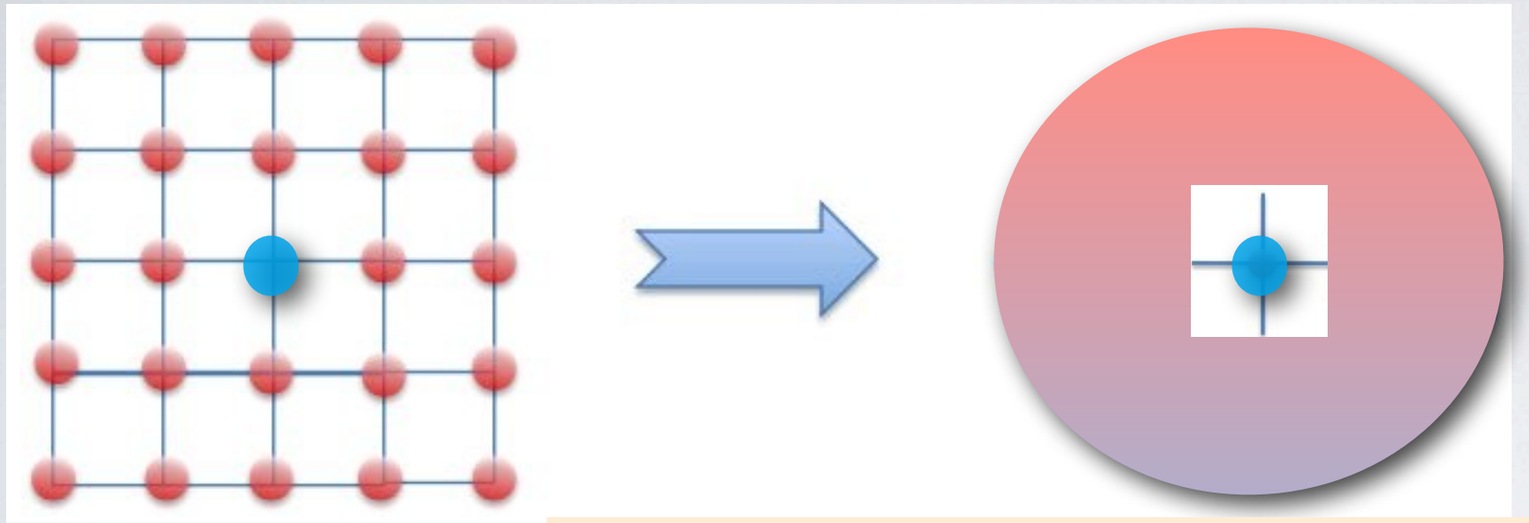
LOCAL DENSITY APPR.

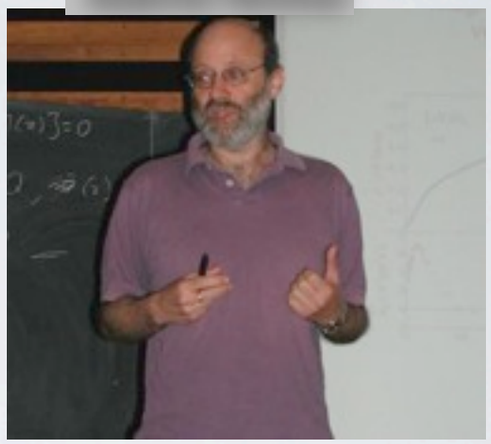


Why is LDA bad when narrow (*d*,*f*) are coexisting with wide (*s*,*p*) states?

LDA potential depends only on the total density, it does not distinguish between states in narrow and wide bands

DYNAMICAL MEAN FIELD





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

Functional integral for the solid: approximated by action local in space (but not time):

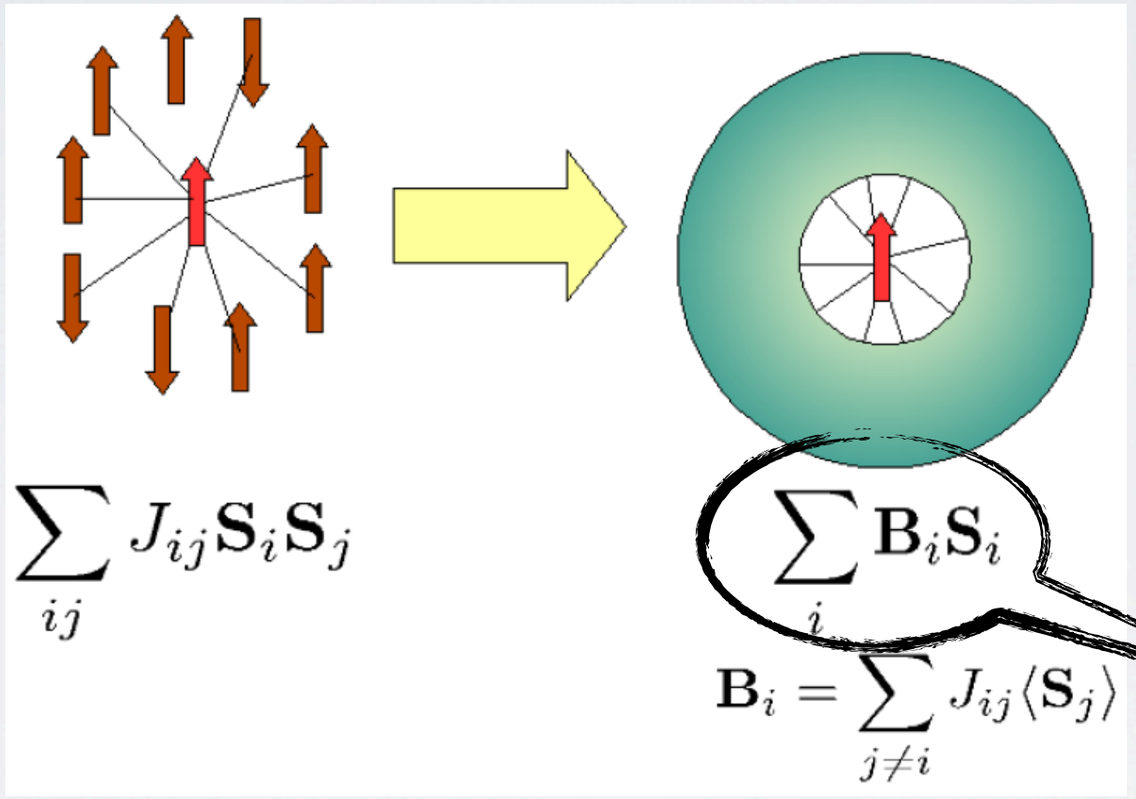
$$Z = \int D[\psi^\dagger \psi] e^{-\sum_i S_{atom}(i) - \sum_{i \neq j} \int d\tau \psi_i^\dagger(\tau) H_{ij} \psi_j(\tau)}$$

$$Z = \int D[\psi^\dagger \psi] e^{-\sum_i S_{atom}(i) - \sum_i \int d\tau \int d\tau' \psi_i^\dagger(\tau) \Delta(\tau - \tau') \psi_i(\tau')}$$

STATIC MEAN FIELD

Weiss mean field theory for spin systems

Exact in the limit of large connectivity z



Simplification:
Local problem!

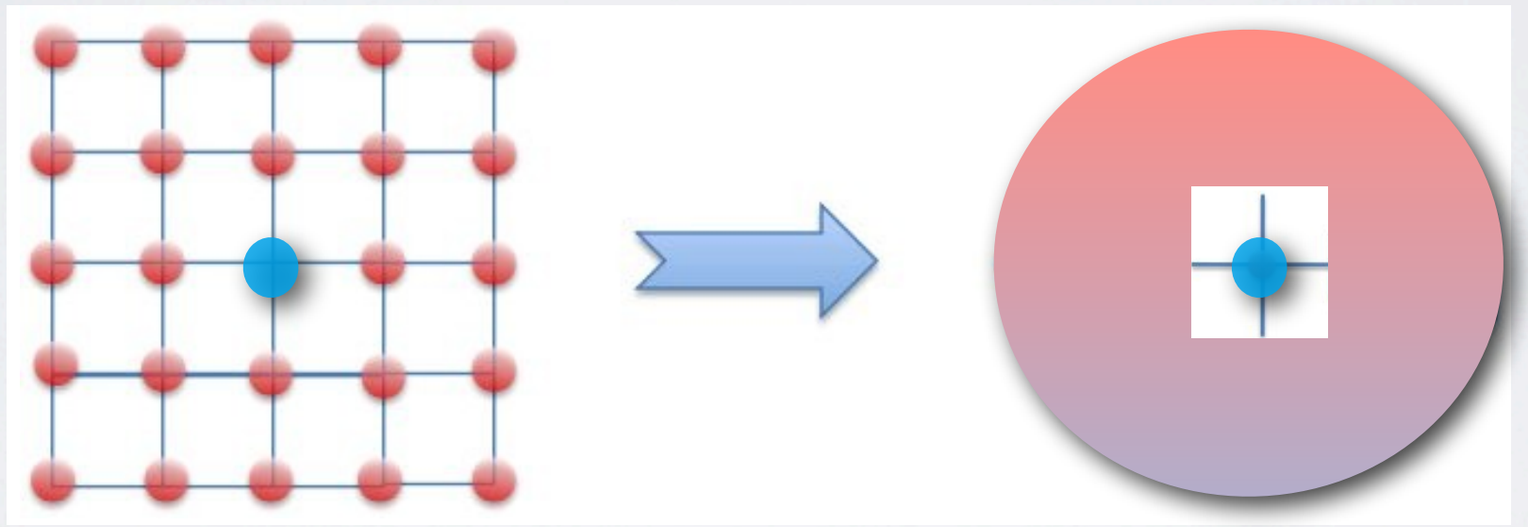
Classical problem of spin in a magnetic field

DMFT SELF CONSIST. C.

$$\left.\begin{aligned} G_{imp} &= G_{ii} \\ \Sigma_{ii} &= \Sigma_{imp} \end{aligned}\right\}$$

SCC for the Hubbard-like model:

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

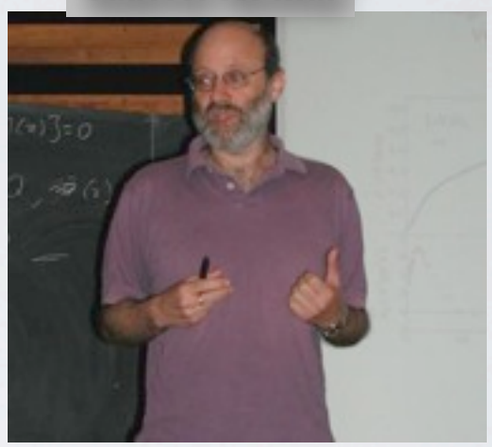


$G_{ii} \quad \Sigma_{ii} \quad U_{ii}$ $\qquad$ $G_{imp} \quad \Sigma_{imp} \quad U_{imp}$

DYNAMICAL MEAN FIELD

Luttinger-Ward Functional:

$$\Gamma[\{G\}] = -\mathrm{Tr}((G_0^{-1} - G^{-1})G) + \mathrm{Tr}\log(-G) + \Phi[\{G\}]$$



DMFT approx: $\Phi[\{G_{ij}\}] \to \sum_i \Phi[\{G_{ii}\}]$

i is site or cluster

: ***all local*** diagrams
(fully dressed propagators)

$\Phi[G_{ii}] =$ 1/2 +1/2 +1/4 +... +...

Sum of *all local* Feynman diagrams

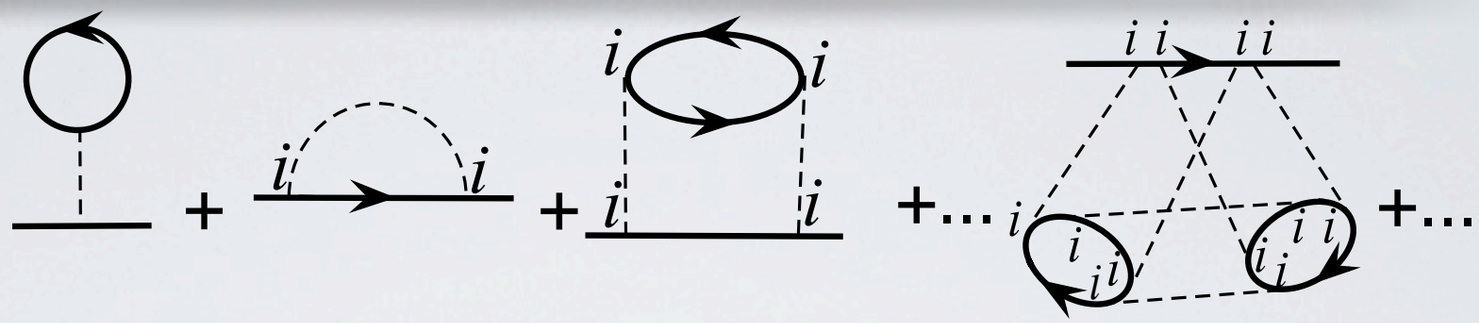
DMFT funcional:

$$\Gamma_{DMFT}[G] = \mathrm{Trlog}\, G - \mathrm{Tr}\left((G_0^{-1} - G^{-1})G\right) + \sum_i \Phi[G_{ii}]$$

known functional

similarity with DFT: $\Phi_{xc}^{LDA} = \int_{\mathbf{r}} \phi_{xc}[\rho(\mathbf{r})]$

DYNAMICAL MEAN FIELD

$$\frac{\delta\Phi[\{G_{ii}]\}}{\delta G_{ii}} =$$ 

To sum this infinite set of diagrams, we turn to the quantum impurity problem!

the same as DMFT functional

Exact action for the impurity problem:

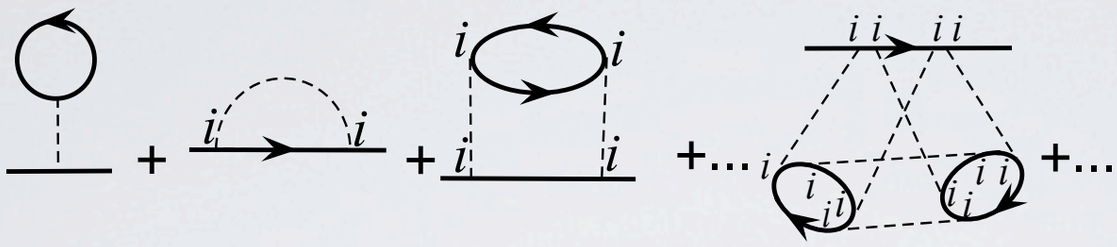
$$\Gamma_{imp}[G_{imp}] = \mathrm{Tr}\log G_{imp} - \mathrm{Tr}\left((G_{0\,imp}^{-1} - G_{imp}^{-1})G_{imp}\right) + \Phi[G_{imp}]$$

with $\Phi[G_{imp}]$ all skeleteon diagrams constructed by

by G_{imp} and U

DMFT SADDLE POINT

The trick to sum the local Feynman diagrams:

$$\frac{\delta\Phi[\{G_{ii}]\}}{\delta G_{ii}} =$$  $$= \frac{\delta\Phi[\{G_{imp}]\}}{\delta G_{imp}}$$

For this to work, we must require: $G_{ii} = G_{imp}$

$U_{ii} = U_{imp}$

The DMFT functional is:

$$\Gamma_{DMFT}[\{G\}] = -\mathrm{Tr}((G_0^{-1} - G^{-1})G) + \mathrm{Tr}\log(-G) + \sum_i \Phi[\{G_{ii}\}]$$

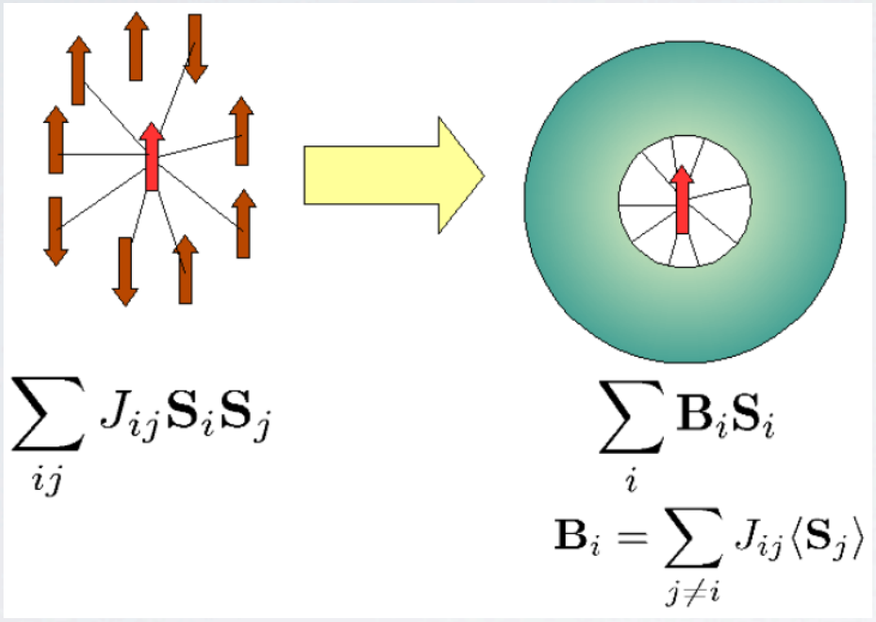
And from saddle point, we get:

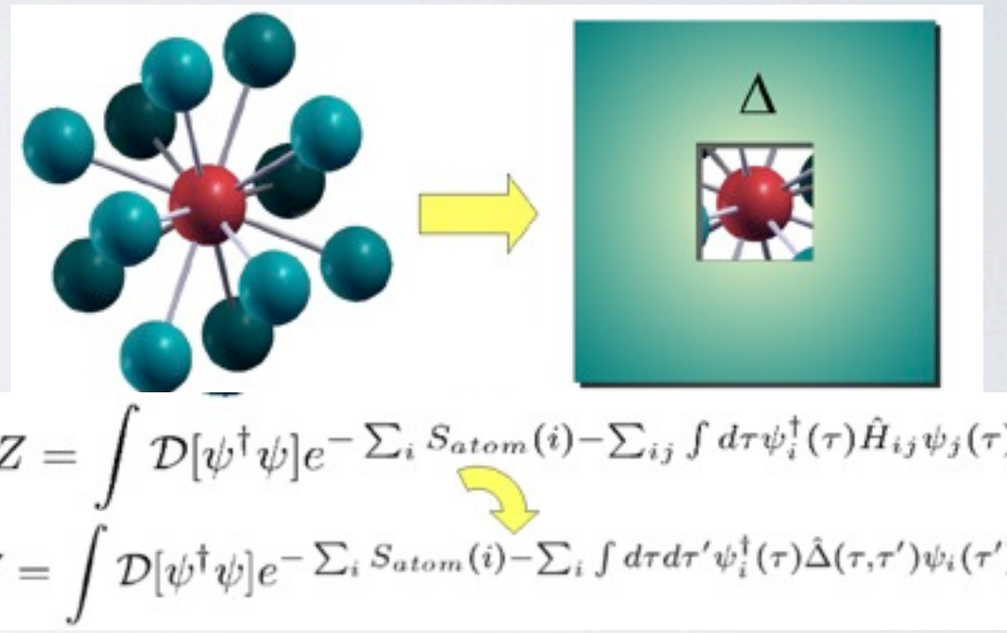
$$\frac{\delta\Gamma_{DMFT}[\{G\}]}{\delta G_{jk}} = -{G_0}^{-1}_{kj} + G^{-1}_{kj} + \frac{\delta\Phi[\{G_{ii}\}]}{\delta G_{ii}}\delta_{j=i}\delta_{k=i} = 0$$

which is equivalent to: $\Sigma^{lattice}_{ii} = \Sigma_{imp}$

HOW LOCAL ARE CORRELATIONS?

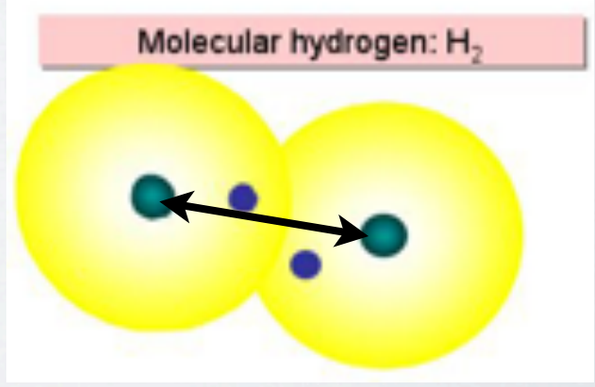
Correlations are only local in large d (large connectivity z) hence DMFT exact -- Weiss mean field theory





What about finite D? What about 0?

H2 molecule:



LOCAL CORRELATIONS

$$G^i_{local} \equiv \hat{P}G(\mathbf{r}-\mathbf{R}_i, \mathbf{r}'-\mathbf{R}_i) = \sum_{\alpha\beta} \chi^*_\alpha(\mathbf{r}) G_{\alpha\beta} \chi_\beta(\mathbf{r}')$$

$\mathbf{R}_i$, vector to the center of atom i

$\mathbf{r}$ vector centered on an atom

Hartree-Fock + DMFT:

$$\Phi[G] \rightarrow E_H[\rho] + E_X[\rho] + \sum_i (\Phi^{DMFT}[G^i_{local}] - E_H[\rho^i_{local}] - E_x[\rho^i_{local}])$$

LDA + DMFT:

$$\Phi[G] \rightarrow E_H[\rho] + E_X[\rho] + \Phi^{LDA}_C[\rho] + \sum_i (\Phi^{DMFT}[G^i_{local}] - E_H[\rho^i_{local}] - E_x[\rho^i_{local}] - \Phi^{LDA}_C[\rho^i_{local}])$$

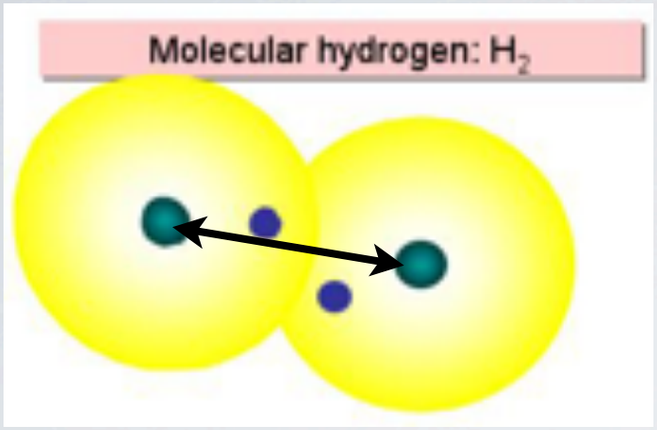
$$E_H[\rho] = \frac{1}{2}\int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \qquad E_H[\rho^i_{local}] = \frac{1}{2}\int \frac{\rho^i_{local}(\mathbf{r})\rho^i_{local}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

$$E_X[\rho] = -\frac{1}{2}\int \frac{\rho^\sigma(\mathbf{r}\mathbf{r}')\rho^\sigma(\mathbf{r}'\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|} \qquad E_X[\rho^i_{local}] = -\frac{1}{2}\int \frac{\rho^{i,\sigma}_{local}(\mathbf{r},\mathbf{r}')\rho^{i,\sigma}_{local}(\mathbf{r}'\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|}$$

$$\Phi^{LDA}_C[\rho] = \int_{\mathbf{r}} \varepsilon_c(\rho(\mathbf{r}))\rho(\mathbf{r}) \qquad \Phi^{LDA}_C[\rho^i_{local}] = \int_{\mathbf{r}} \varepsilon_c(\rho^i_{local}(\mathbf{r}))\rho^i_{local}(\mathbf{r})$$

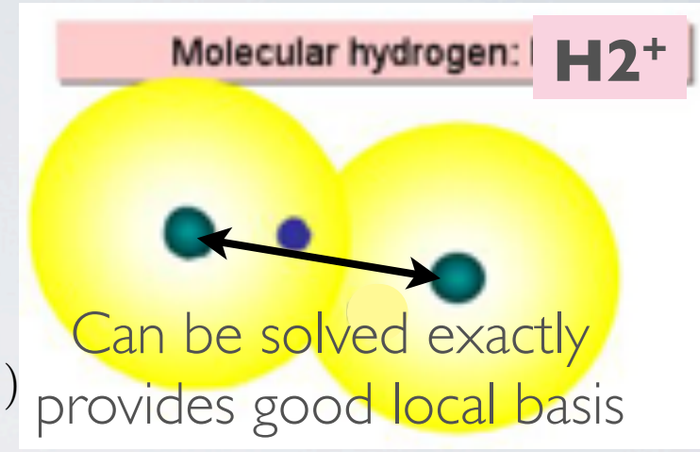
TEST THE IDEA: H2 MOLECULE

Archetypal problem of strong correlations:



$$G^i_{local}\,?$$

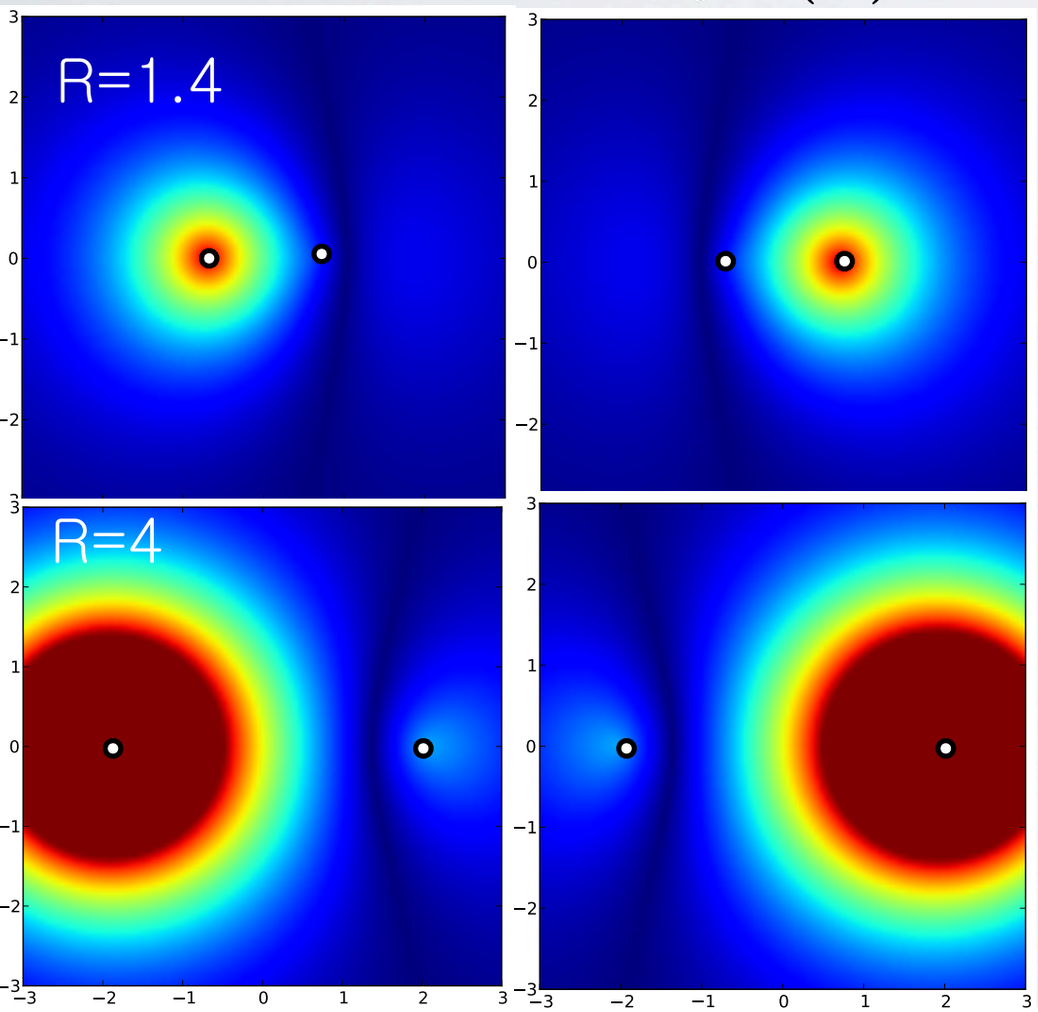
$$G^L_{local} \equiv \chi^*_L(\mathbf{r})\,\langle\chi_L|\,G\,|\chi_L\rangle\,\chi_L(\mathbf{r}')$$
$$G^R_{local} \equiv \chi^*_R(\mathbf{r})\,\langle\chi_R|\,G\,|\chi_R\rangle\,\chi_R(\mathbf{r}')$$

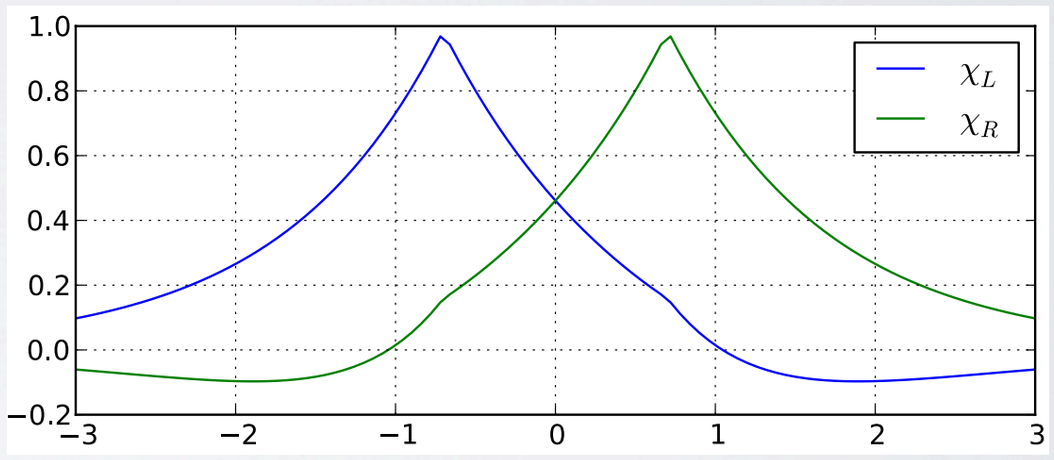


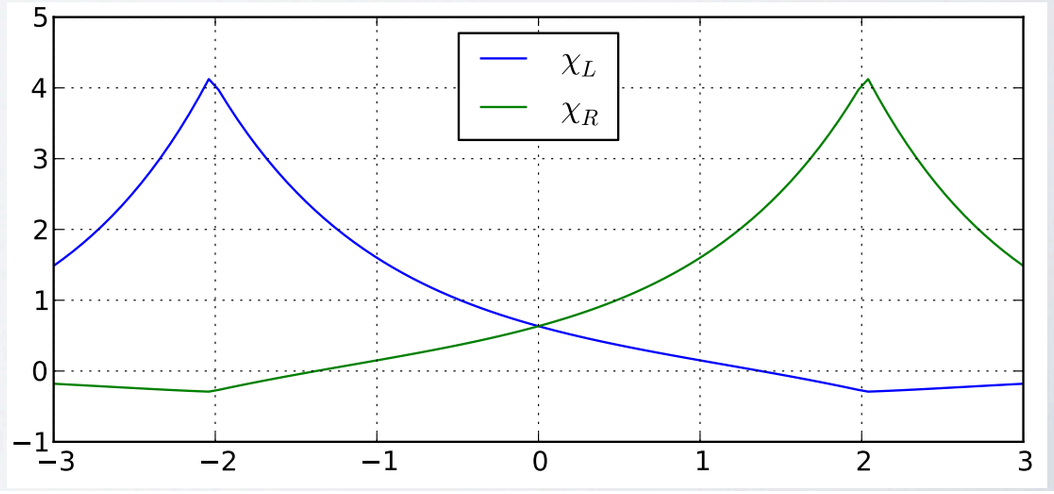
$$\chi_L(\mathbf{r}) = \frac{1}{\sqrt{2}}(|1\sigma_g(H^+)\rangle - |1\sigma_u(H^+)\rangle)$$

$\chi_L(\mathbf{r})$ $\chi_R(\mathbf{r})$

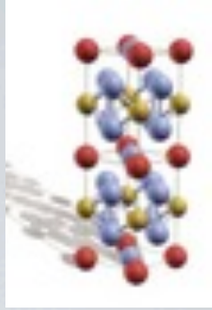
$$\chi_R(\mathbf{r}) = \frac{1}{\sqrt{2}}(|1\sigma_g(H^+)\rangle + |1\sigma_u(H^+)\rangle)$$



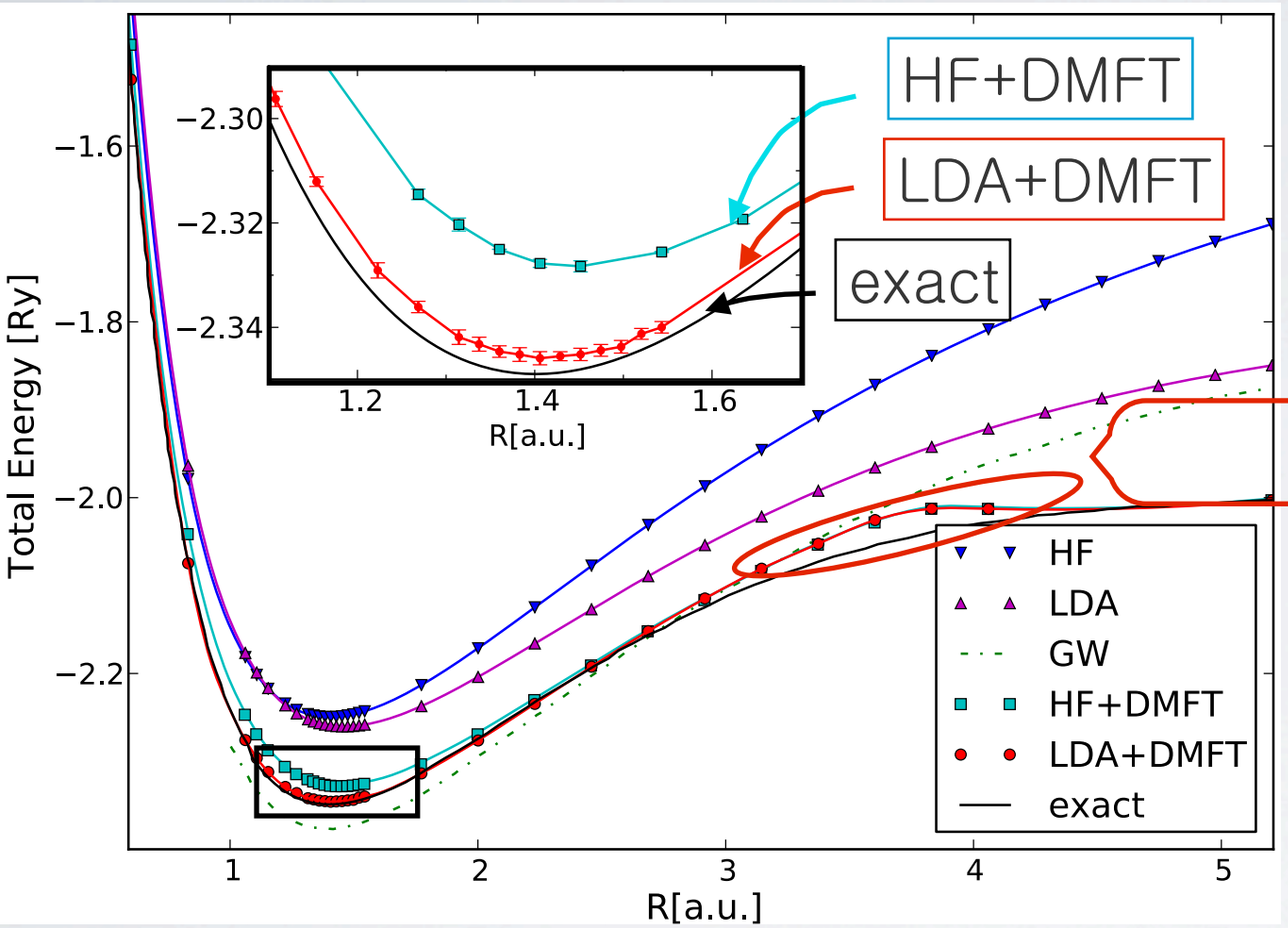




DMFT+ for H2 molecule

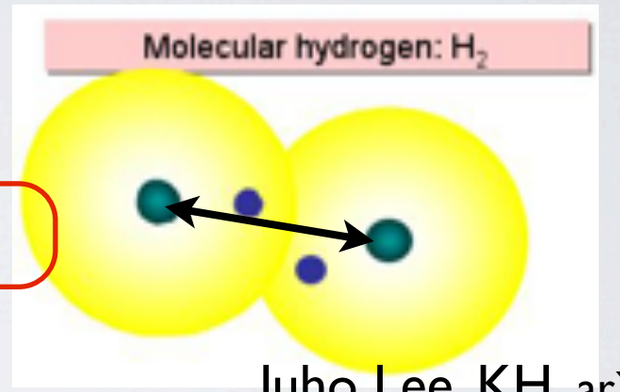


Archetypal problem of strong correlations:



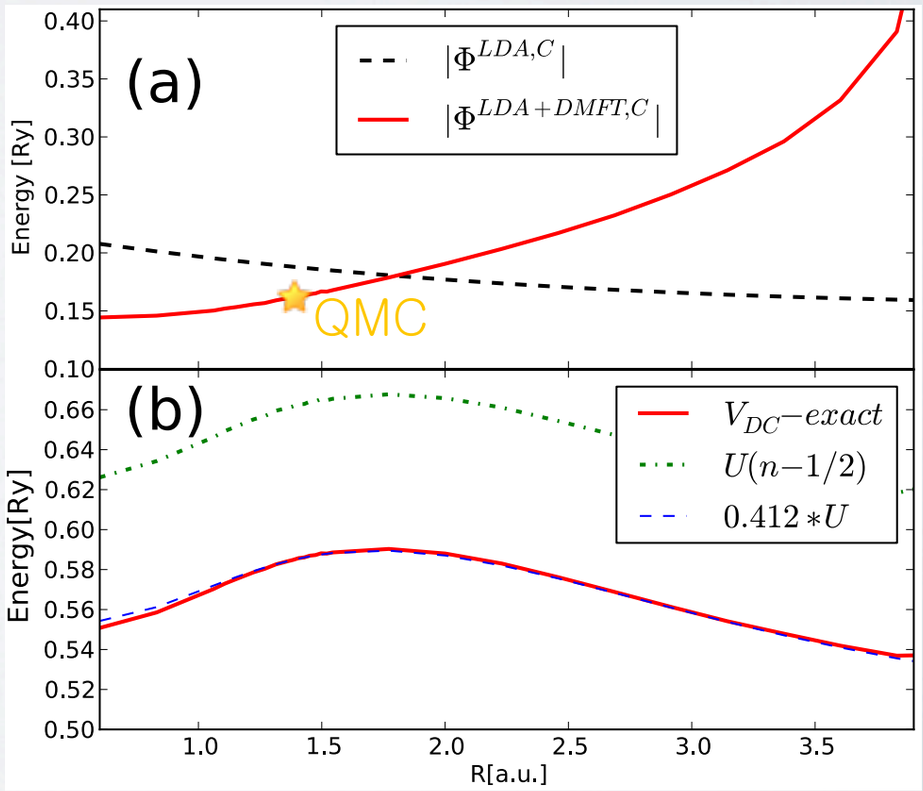
DMFT exact in ∞ D, or large connectivity Z
It is not expected to be good for H2 molecule

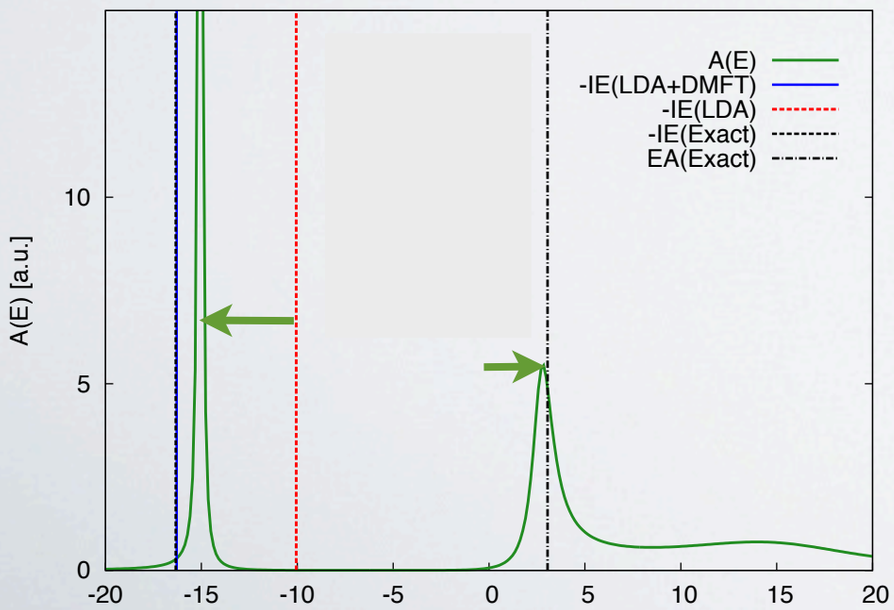
need cluster corrections



Juho Lee, KH, arXiv:1403.2474

Error of total energy using LDA+DMFT <0.2%!





improves ionization energy of LDA

correlation energy increases with R (LDA wrong trend)

double-counting smaller than phenomenological formula

SPECTRAL DENSITY FUNCT.T.

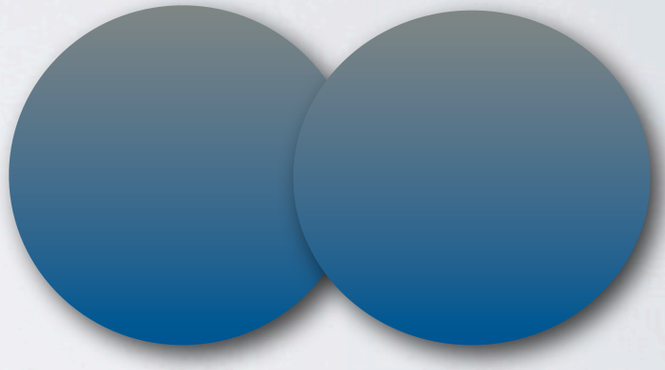
In solids, we need further approximations.

Too many functions needed for accurate description of GF.

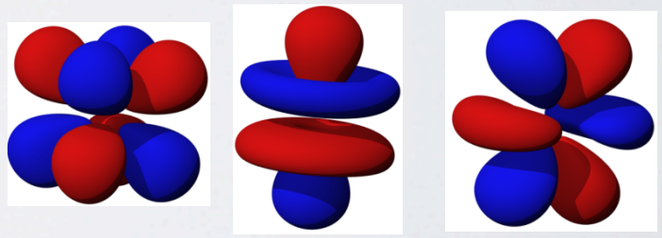
$$G(\mathbf{r}-\mathbf{R}_i,\mathbf{r}'-\mathbf{R}_i)=\sum_{\alpha\beta}\chi_\alpha(\mathbf{r})G_{\alpha\beta}\chi_\beta(\mathbf{r}')$$

Horrendous impurity problem!

Itinerant states (*sp*) are very economically described by LDA.

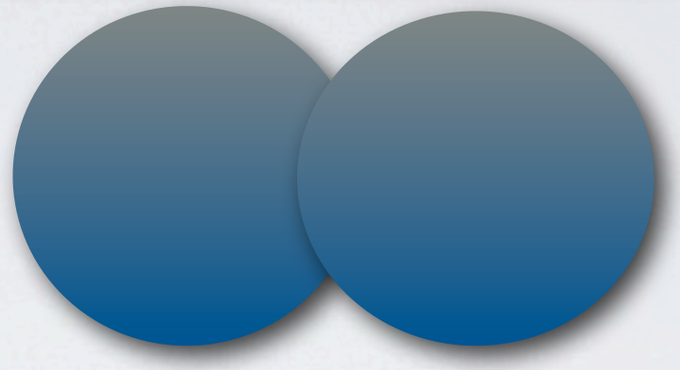


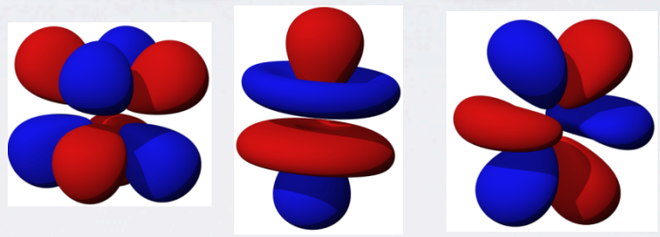
Narrow states (*df*) are much better described by DMFT



SCREENING IN SOLIDS

Since we remove some itinerant states from the DMFT, they screen DMFT Coulomb interaction



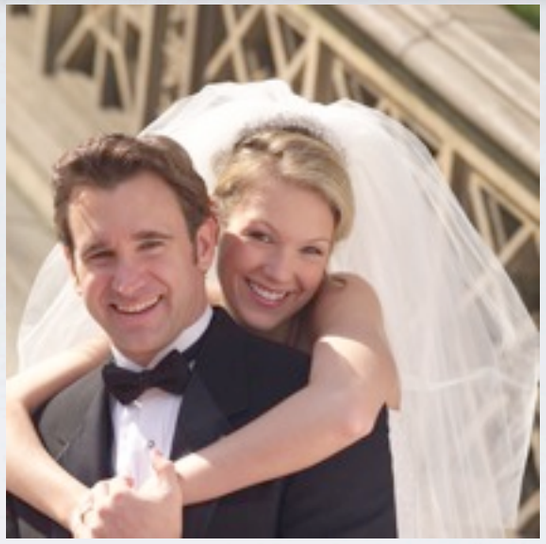


effective U smaller than 1/|r-r'|

Effective U depends on the type of model (which states are included/ excluded in DMFT.)

DFT+DMFT

Very happy marriage:



$$\Phi[G] \rightarrow \Phi^{LDA}[\rho] + \sum_{i \in corr.\ atoms} (\Phi^{DMFT}[G^i_{local}] - \Phi^{DC}[\rho^i_{local}])$$

Sum of all skeleton diagrams for "most" correlated states (d or f)

LDA functional

(depends only on the total density locally in 3D-space, functional known only approximately)

DMFT approximation for the LDA functional

DFT+DMFT

DMFT is very expensive!

Can treat:

- 5 orbitals (for transition metal ions)
- 7 orbitals (for lanthanides&actinides)

Important virtues of DMFT:

- Local theory (to correlated ion) → Scales linearly with the system size

  For large unit cell (50atoms+), DFT can be slower than DMFT!

- Can hybridize with arbitrary number of itinerant states (can integrate out itinerant states) → No need to approximate DFT bands structure

TWO ROUTES

How to marry DFT and DMFT?

$\rho(\mathbf{r}), -\nabla^2 + V_{ext}(\mathbf{r}) + V_{xc}(\mathbf{r})$ + $G^{DMFT}_{i\alpha,i\beta}, \Sigma^{DMFT}_{i\alpha,i\beta}$

Downfolding to small window Wannier functions

approximates kinetic energy by a few hopping matrix elements
Not very localized corr. states

$$-\nabla^2 + V_{ext}(\mathbf{r}) + V_{xc}(\mathbf{r}) \rightarrow t^{\alpha\beta}_{ij}$$

$$G_{i\alpha,i\beta} = \sum_{\mathbf{k}} (i\omega + \mu + t_{\mathbf{k}} - \Sigma)^{-1}_{\alpha,\beta}$$

Conceptually simple (model hamiltonian) but local approximation in this Wannier basis questionable!

Projection & Embedding

embedding self-energy to the large Hilbert space very localized corr. states

$$\hat{E}\,\Sigma^{DMFT}_{i\alpha,i\beta} \rightarrow \Sigma(\mathbf{r},\mathbf{r}')$$

$$G(\mathbf{r},\mathbf{r}') = (i\omega + \mu + \nabla^2 - V_{ext}(\mathbf{r}) - V_{xc}(\mathbf{r}) - \hat{E}\,\Sigma^{DMFT})^{-1}$$

$$G^{DMFT}_{i\alpha,i\beta} = \hat{P}\,G(\mathbf{r},\mathbf{r}')$$

Kinetic energy treated exactly, local approximation very good computationally *not* more expensive

TWO ROUTES

Projection & Embedding

$$\begin{pmatrix} G^{cc}, G^{cr} \\ G^{rc}, G^{rr} \end{pmatrix} = \sum_{\mathbf{k}} \left(\begin{array}{c|c} i\omega + \mu + H^{cc}_{\mathbf{k}} - \Sigma & -V^{cr}_{\mathbf{k}} \\ \hline -V^{rc\dagger}_{\mathbf{k}} & i\omega + \mu - H^{rr}_{\mathbf{k}} \end{array} \right)^{-1}$$

Downfolding via Wannier functions:

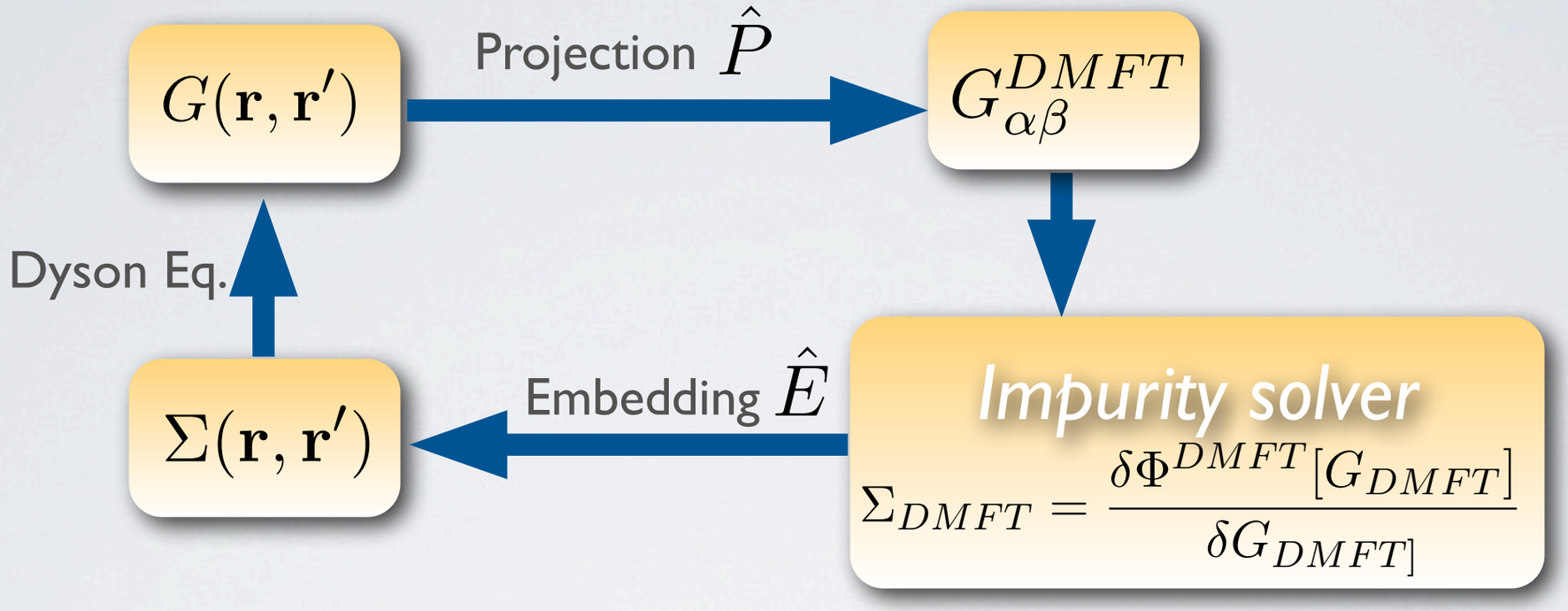
$$G^{cc} = \sum_{\mathbf{k}} (i\omega + \mu + \widetilde{H}^{cc}_{\mathbf{k}} - \Sigma)^{-1}$$

$H^{rr}_{\mathbf{k}}$ can have arbitrary large dimension
but it can be exactly integrated out
in impurity model

Only G^{cc} is needed in DMFT

The number of correlated states has to be small
while the part treated by DFT can be arbitrary large

PROJECT/EMBED



also needs local $\hat{U}$ *(later)*

Projection: $G^{DMFT}_{\alpha\beta} = \int\int d\mathbf{r}d\mathbf{r}' P(\alpha\beta,\mathbf{r}\mathbf{r}')G(\mathbf{r},\mathbf{r}')$

Embedding: $\Sigma(\mathbf{r},\mathbf{r}') = \sum_{\alpha\beta} E(\mathbf{r}\mathbf{r}',\alpha\beta)\Sigma_{\alpha\beta}$

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

DFT+DMFT

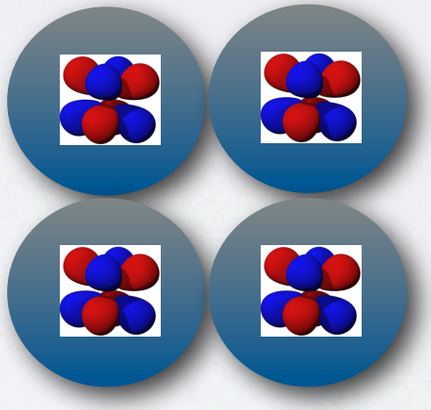
DFT+DMFT functional:

$$\Gamma[\{G\}] = -\mathrm{Tr}((G_0^{-1} - G^{-1})G) + \mathrm{Tr}\log G + \Phi^{LDA}[\{\rho\}] + \Phi^{DMFT}[\{G_{loc}\}] - \Phi^{DC}[\{\rho_{loc}\}]$$

$$G_0^{-1} = -\frac{\partial}{\partial\tau} + \mu + \nabla^2 - V_{ext}$$

$$G_{loc\,i}(\mathbf{r}\,t, \mathbf{r}'\,t') = \hat{P}_i G(\mathbf{r}\,t, \mathbf{r}'\,t')$$ local to the atom and orbital "*i*" but dynamic

$$\rho(\mathbf{r}) = \delta(\mathbf{r} - \mathbf{r}')\delta(t - t')G(\mathbf{r}\,t, \mathbf{r}'\,t')$$ static and equal space component



$\hat{P}_i$ projection

$\hat{P}_i^{-1} \equiv \hat{E}_i$ embedding

Saddle point Eq.:

$$\frac{\delta\Gamma[\{G\}]}{\delta G} = -G_0^{-1} + G^{-1} + \delta(\mathbf{r} - \mathbf{r}')\delta(t - t')\frac{\delta\Phi^{LDA}[\{\rho\}]}{\delta\rho} + \hat{P}^{-1}\frac{\delta\Phi^{DMFT}[\{G_{loc}\}]}{\delta G_{loc}} + \delta(\mathbf{r} - \mathbf{r}')\delta(t - t')P^{-1}\frac{\delta\Phi^{DC}[\{\rho_{loc}\}]}{\delta\rho_{loc}}$$

SADDLE POINT EQ.: DFT+DMFT

$$G_0^{-1} - G^{-1} = \delta(\mathbf{r}-\mathbf{r}')\delta(t-t')\frac{\delta\Phi^{LDA}[\{\rho\}]}{\delta\rho} + \hat{P}^{-1}\frac{\delta\Phi^{DMFT}[\{G_{loc}\}]}{\delta G_{loc}} + \delta(\mathbf{r}-\mathbf{r}')\delta(t-t')P^{-1}\frac{\delta\Phi^{DC}[\{\rho_{loc}\}]}{\delta\rho_{loc}}$$

$$V_{int} \equiv \delta(\mathbf{r}-\mathbf{r}')\delta(t-t')\frac{\delta\Phi^{DFT}(\rho)}{\delta\rho} = \delta(\mathbf{r}-\mathbf{r}')\delta(t-t')(V_{Hartree}+V_{xc})$$

Hartree+XC-potential just like in LDA

$$\Sigma^{DMFT} \equiv \hat{P}^{-1}\frac{\delta\Phi^{DMFT}[G_{loc}]}{\delta G_{loc}}$$

Embedded sum of all local diagrams (just like in DMFT)

$$V_{dc} \equiv \delta(\mathbf{r}-\mathbf{r}')\delta(t-t')\hat{P}^{-1}\frac{\delta\Phi^{DC}[\rho_{loc}]}{\delta\rho_{loc}}$$

double-counting

Functional can be cast into stationary functional of 2x2 variables:

$$\Gamma[\rho, V_{int}, G_{loc}, \Sigma^{DMFT}] = -\mathrm{Tr}\log(-\frac{\partial}{\partial\tau} + \mu + \nabla^2 - V_{ext} - V_{int} - \Sigma^{DMT} + V_{dc}) +$$

usual parametrization of XC from the electron gas

$$+\Phi^{LDA}[\rho] - \mathrm{Tr}(V_{int}\rho) +$$

from solution of a quantum impurity problem

$$+\Phi^{DMFT}[G_{loc}] - \mathrm{Tr}(\Sigma^{DMFT}G_{loc}) -$$

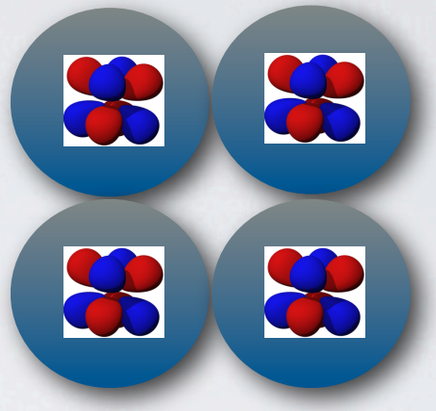
double-counting

$$-\Phi_{dc}(\rho_{loc}) + \mathrm{Tr}(V_{dc}\rho_{loc})$$

PROJECT/EMBED: WHAT IS

Definition of projection:

$$G^{loc}_{\alpha\beta} = \int\int d\mathbf{r}d\mathbf{r}' P(\alpha\beta, \mathbf{r}'\mathbf{r}) G(\mathbf{r}, \mathbf{r}')$$



$\hat{P}_i$ projection

$\hat{P}_i^{-1} \equiv \hat{E}_i$ embedding

Saddle point Eq. give connection between P & E:

$$\frac{\delta\Phi^{DMFT}[\{G^{loc}_{\alpha'\beta'}\}]}{\delta G(\mathbf{r}, \mathbf{r}')} = \sum_{\alpha\beta} \frac{\delta\Phi^{DMFT}[\{G^{loc}_{\alpha'\beta'}\}]}{\delta G^{loc}_{\alpha\beta}} \frac{\delta G^{loc}_{\alpha\beta}}{\delta G(\mathbf{r}, \mathbf{r}')} = \sum_{\alpha\beta} \frac{\delta\Phi^{DMFT}[\{G^{loc}_{\alpha'\beta'}\}]}{\delta G^{loc}_{\alpha\beta}} P(\alpha\beta, \mathbf{r}'\mathbf{r})$$

Definition of Embedding is:

$$\Sigma(\mathbf{r}, \mathbf{r}') \equiv \sum E(\mathbf{r}\mathbf{r}', \alpha\beta)\Sigma$$

Hence the Embedding is:

$$E(\mathbf{r}\mathbf{r}', \alpha\beta) = P(\alpha\beta, \mathbf{r}'\mathbf{r})$$

We need to define Projection operator only!

hence:

$$\Sigma(\mathbf{r}, \mathbf{r}') = \sum \Sigma \quad P(\alpha\beta, \mathbf{r}'\mathbf{r})$$

PROJECT/EMBED

Properties of projection/embeding

first embed $\Sigma(\mathbf{r},\mathbf{r}') = \sum_{\alpha\beta} \Sigma_{\alpha\beta}\ P(\beta\alpha,\mathbf{r}'\mathbf{r})$

then project $\Sigma_{\alpha\beta} = \int\int P(\quad,\mathbf{r}'\mathbf{r})\Sigma(\mathbf{r},\mathbf{r}')d\mathbf{r}d\mathbf{r}'$

$\hat{P} * \hat{E} = I$

first project $\int\int \quad \mathbf{r}'\mathbf{r} \quad \mathbf{r}\ \mathbf{r}' \quad \mathbf{r}\ \mathbf{r}'$

then embed $\mathbf{r}\ \mathbf{r}' \quad \sum_{\alpha\beta} \quad \alpha\beta \quad \mathbf{r}'\mathbf{r}$

$\hat{E} * \hat{P} \neq I$

$(\hat{E} * \hat{P}) * (\hat{E} * \hat{P}) = \hat{E} * \hat{P}$

Property of a true projector

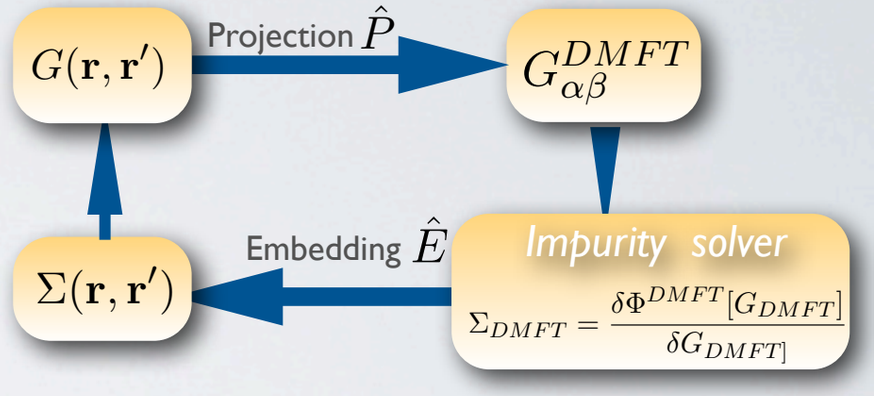
Projected local Green's function: $G_{local}(\mathbf{r},\mathbf{r}') = \hat{E} * \hat{P} G(\mathbf{r},\mathbf{r}')$

REQUIREMENT FOR CAUSAL DMFT EQ.

DMFT SCC:

$$G_{imp} = \frac{1}{\omega - E_{imp} - \Sigma - \Delta} = \hat{P}\frac{1}{\omega + \nabla^2 - V_{ext} - V_H - V_{xc} - \hat{E}(\Sigma - V_{dc})} = G_{local}$$

$$\Sigma \to i\infty$$



Additional requirement for causal DMFT

$$\int_{\mathbf{r}\mathbf{r}'} P(\alpha\beta,\mathbf{r}\mathbf{r}')\Big(\sum_{\alpha'\beta'} E(\mathbf{r}\mathbf{r}',\beta'\alpha')\Sigma_{\alpha'\beta'}\Big)^{-1}_{\mathbf{r}'\mathbf{r}} = \Sigma_{\alpha\beta} \qquad \left(\ \hat{P}\frac{1}{\hat{E}} = I\ \right)$$

If projection separable: $P(\alpha\beta,\mathbf{r}\mathbf{r}') = U^{\dagger}(\alpha\mathbf{r})U(\mathbf{r}'\beta)$

requirement satisfied $\hat{P}\frac{1}{\hat{E}} = U^{\dagger}(\alpha\mathbf{r})U^{\dagger\,-1}(\mathbf{r}\alpha')U^{-1}(\beta'\mathbf{r}')U(\mathbf{r}'\beta) = I$

REQUIREMENT FOR STATIONARITY (ENERGY)

Projector should not depend on the solution

Return to definition of projector:

$$G^{loc}_{\alpha\beta} = \int\int d\mathbf{r}d\mathbf{r}' P(\alpha\beta, \mathbf{r}'\mathbf{r})\, G(\mathbf{r}, \mathbf{r}')$$

Return to saddle point Eq.:

$$\frac{\delta\Phi^{DMFT}[\{G^{loc}_{\alpha'\beta'}\}]}{\delta G(\mathbf{r},\mathbf{r}')} = \sum_{\alpha\beta} \frac{\delta\Phi^{DMFT}[\{G^{loc}_{\alpha'\beta'}\}]}{\delta G^{loc}_{\alpha\beta}} \frac{\delta G^{loc}_{\alpha\beta}}{\delta G(\mathbf{r},\mathbf{r}')} = \sum_{\alpha\beta} \frac{\delta\Phi^{DMFT}[\{G^{loc}_{\alpha'\beta'}\}]}{\delta G^{loc}_{\alpha\beta}} P(\alpha\beta, \mathbf{r}'\mathbf{r})$$

Here we implicitly assumed that $\dfrac{\delta P}{\delta G} = 0$

POSSIBLE PROJECTORS

Wannier orbitals: $$|W_{\mathbf{k}\alpha}\rangle = \sum_{i \in LowE} |\psi_{i\mathbf{k}}\rangle \langle \psi_{i\mathbf{k}}| \, |\chi_{\alpha'}\rangle \frac{1}{\sqrt{\sum_j \langle \chi_\alpha | \, |\psi_{\mathbf{k}j}\rangle \langle \psi_{\mathbf{k}j}| \, |\chi_{\alpha'}\rangle}}$$

$$P(\alpha\beta, \mathbf{r}\mathbf{r}') = \sum_{\mathbf{k}} W^*_{\mathbf{k}\alpha}(\mathbf{r}) W_{\mathbf{k}\beta}(\mathbf{r}')$$

$\psi_{i\mathbf{k}}$ KS orbitals

χ_α localized orbitals

Stationarity: $$\frac{\delta P}{\delta G} = 0$$ 

LDA+U projector: $$P^0(lm, lm', \mathbf{r}\mathbf{r}') = Y_{lm}(\hat{\mathbf{r}}) \delta(r - r') Y_{lm'}(\hat{\mathbf{r}}')$$

Causal DMFT equations: $$\int_{\mathbf{r}\mathbf{r}'} P(\alpha\beta, \mathbf{r}\mathbf{r}') (\sum_{\alpha'\beta'} E(\mathbf{r}\mathbf{r}', \beta'\alpha') \Sigma_{\alpha'\beta'})^{-1}_{\mathbf{r}'\mathbf{r}} = \Sigma_{\alpha\beta} \qquad \left(\hat{P} \frac{1}{\hat{E}} = I \right)$$ 

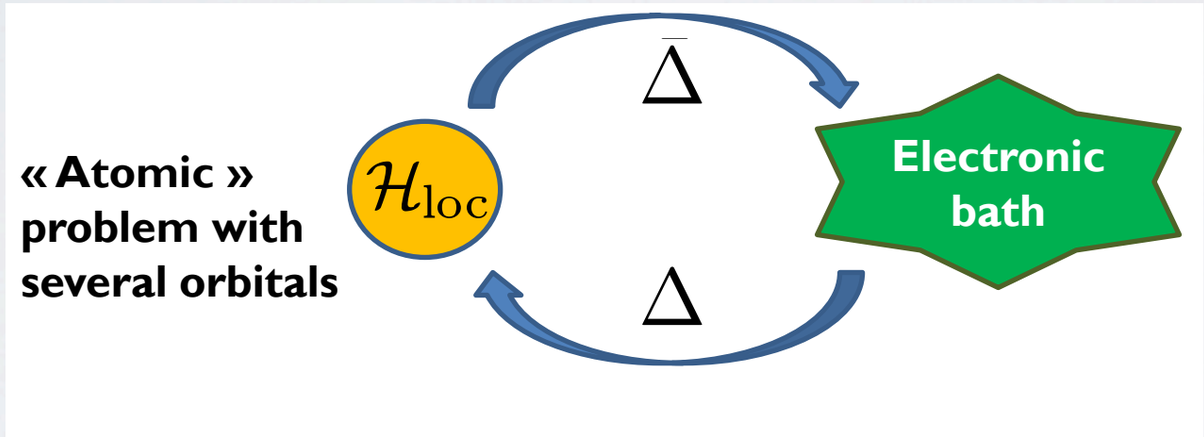
Possible choice: $$P(lm, lm', \mathbf{r}\mathbf{r}') = Y_{lm}(\hat{\mathbf{r}}) R^{LDA}_l(\mathbf{r}) R^{LDA}_l(\mathbf{r}') Y_{lm'}(\hat{\mathbf{r}}')$$ 

IMPURITY SOLVER: $\Sigma_{DMFT} = \frac{\delta \Phi^{DMFT}[G_{DMFT}]}{\delta G_{DMFT}]}$

LW functional:

$$\Gamma_{imp}[\{G_{imp}\}] = \mathrm{Tr}\log\left(-G_{imp}\right) - \mathrm{Tr}\left((i\omega - \varepsilon_{imp} - \Delta)G_{imp}\right) + \Phi^{imp}[\{G_{imp}\}]$$

with $\Phi[G_{imp}]$ sum of all skeleteon diagrams.



In the DMFT solution we can compute also the free energy:

$$F^{DFT+DMFT} = \mathrm{Tr}\log(G) - \mathrm{Tr}\log(G_{imp}) + F_{imp} + E^{H}[\rho] + \Phi^{xc}[\rho] - \mathrm{Tr}((V_H + V_{xc})\rho)$$
$$- \Phi^{DC}[\rho_{loc}] + \mathrm{Tr}(V_{dc}\rho_{local})$$

where:

$$F_{imp} = E_{imp} - TS_{imp}$$
$$E_{imp} = \mathrm{Tr}\left(\left(\Delta + \varepsilon_{imp} - \omega_n \frac{\partial \Delta}{\partial \omega_n}\right) G_{imp}\right) + \frac{1}{2}\mathrm{Tr}(\Sigma_{imp} G_{imp})$$

CONTINUOUS TIME QMC

Method of choice for DFT+DMFT: CTQMC in hybridization

P. Werner, PRL (2007); N. Rubtsov PRB 72, 35122 (2005); K.H. Phys. Rev. B 75, 155113 (2007) ;

General impurity problem:

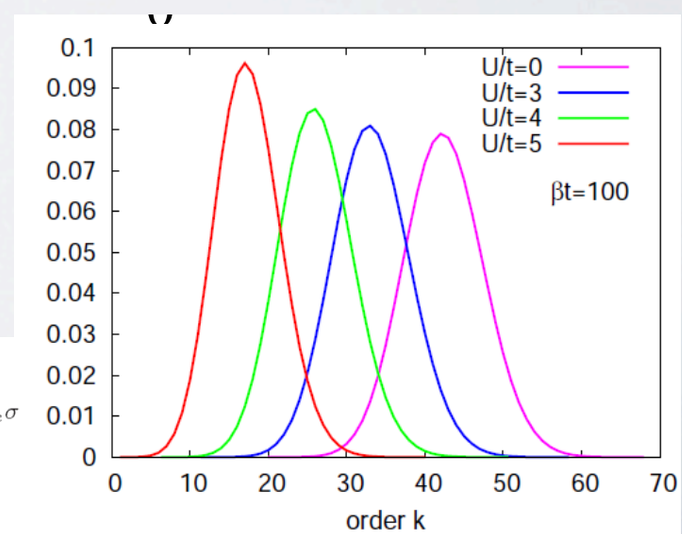
$$Z = \int D[\psi^\dagger \psi] e^{-S_{atom} - \int_0^\beta d\tau \int_0^\beta d\tau' \sum_{\alpha\alpha'} \psi^\dagger_\alpha(\tau)\Delta(\tau-\tau')\psi_{\alpha'}(\tau')}$$

Power expansion in terms Δ, gives series of Feynman diagrams:

$$Z = Z_{atom} \sum_k \frac{1}{k!} \int_0^\beta d\tau_1 \int_0^\beta d\tau_1' \cdots \int_0^\beta d\tau_k \int_0^\beta d\tau_k' \sum_{\alpha_1\alpha_1',\alpha_2,\alpha_2',\cdots\alpha_k\alpha_k'} \langle T_\tau \psi_{\alpha_1'}(\tau_1')\psi^\dagger_{\alpha_1}(\tau_1)\cdots\psi_{\alpha_k'}(\tau_k')\psi^\dagger_{\alpha_k}(\tau_k)\rangle_{atom} \times$$

$$\frac{1}{k!}\mathrm{Det}\begin{pmatrix} \Delta_{\alpha_1\alpha_1'}(\tau_1,\tau_1') & \Delta_{\alpha_2\alpha_2'}(\tau_2,\tau_2') & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots \\ \Delta_{\alpha_k\alpha_1'}(\tau_k,\tau_1') & \cdots & \cdots & \Delta_{\alpha_k\alpha_k'}(\tau_k,\tau_k') \end{pmatrix}$$

Metropolis sampling over the diagrams, very efficient because perturbation order is Gaussian in order *k* peaked at K/T.



Virtues:

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

$$H_{Hubbard+Hunds} = \sum_{L_i,m,\sigma\sigma'} \sum_{k=0}^{2l} \frac{4\pi F^k_{\{l\}}}{2k+1} \langle Y_{L_a}|Y_{km}|Y_{L_c}\rangle\langle Y_{L_d}|Y_{km}|Y_{L_b}\rangle f^\dagger_{L_a\sigma} f^\dagger_{L_b\sigma'} f_{L_d\sigma'} f_{L_c\sigma}$$

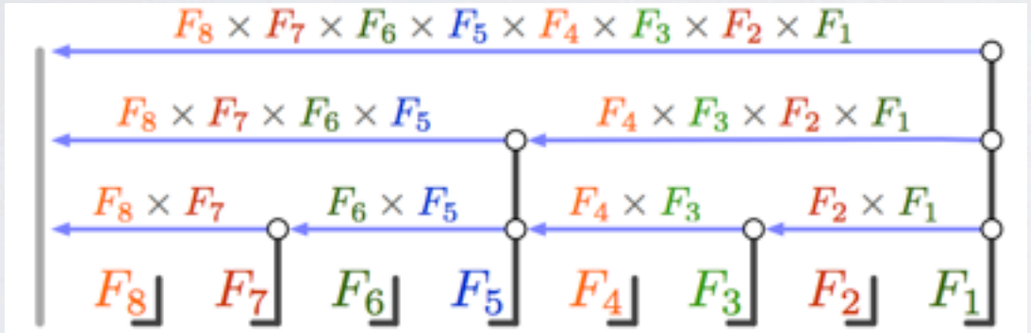
$$H_{SO} = \sum \xi \frac{1}{2}[j(j+1) - l(l+1) - \frac{3}{4}] C^{jm_j}_{lm,\sigma} C^{jm_j}_{lm',\sigma'} f^\dagger_{lm\sigma} f_{lm'\sigma'}$$

BEST ALGORITHM FOR CTQMC

Lazy-Skip list implementation

arXiv: 1403.7214, P. Semon, C.H.-Yee, K.H., A.M. Tremblay

Skip-list:



Like transportation infrastructure, each layer has some extra **express lanes** for faster updates : update time of the order of log(N)

Lazy evaluation of trace:

expensive part: $Trace = \mathrm{Tr}(e^{-\Delta\tau_1 H}\psi_1^\dagger e^{-\Delta\tau_2 H}\psi_2 e^{-\Delta\tau_3 H}\psi_3^\dagger \cdots e^{-\Delta\tau_N H})$

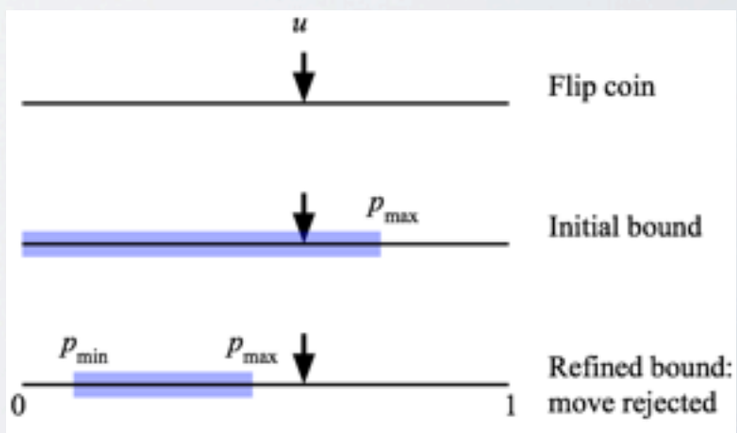
if nonzero, all have norm close to 1 $|\psi| \lesssim 1$

Either very large or very small

$e^{-H\beta} \gg 1 \quad e^{-H\beta} \ll 1$

simple estimate of upper bound $Trace < dim * e^{-\sum_i \Delta\tau_i E_i^{atom}}$

recursively can estimate better and better bound $A < Trace < B$



DOUBLE COUNTING

$$\Phi[G] = \Phi^{LDA}[\rho] + \sum_{i \in corr} \Phi^{DMFT}[G^i_{local}] - \Phi^{DC}[\rho^i_{local}]$$

LDA functional

Sum of all skeleton diagrams local to correlated ions

DMFT approximation of the LDA functional replacing

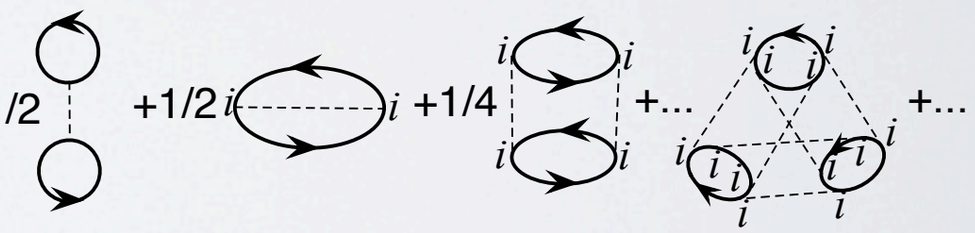
$\rho \to \rho_{local}$

$\hat{V}_C \to \hat{U}_C$

LDA: $\Phi[G, \hat{V}_C] \to \Phi^{LDA}[\rho, \frac{1}{|\mathbf{r}-\mathbf{r}'|}]$

with $\Phi^{LDA}[\rho, \frac{1}{|\mathbf{r}-\mathbf{r}'|}] = \frac{1}{2}\int\int d\mathbf{r}d\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + \int d\mathbf{r}\rho(\mathbf{r})\varepsilon_{xc}(\rho(\mathbf{r}), \frac{1}{|\mathbf{r}-\mathbf{r}'|})$

DMFT: $\Phi[G, \hat{V}_C] \to \Phi[G_{local}, \hat{U}_C]$

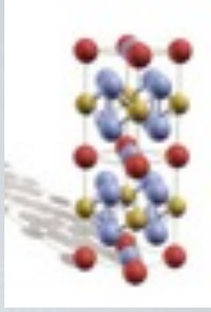
$\Phi[G_{ii}] =$ 

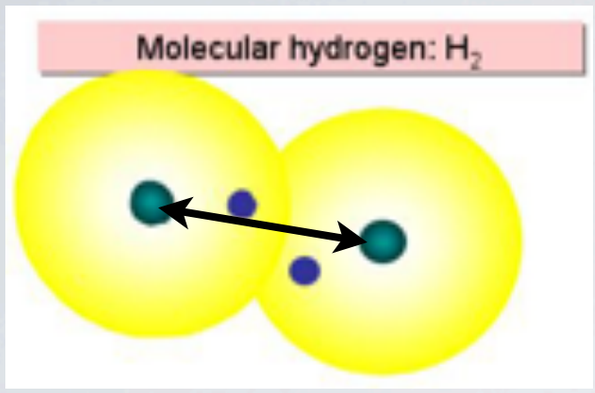
use all graps (just like in exact solution) but use only G_{ii} and U_C instead of full G *and* V_C

intersection: $\Phi^{DC}(\rho_{local}) = E_H[\rho_{local}, \hat{U}_C] + \int d\mathbf{r}\rho_{local}(\mathbf{r})\varepsilon_{xc}(\rho_{local}(\mathbf{r}), \hat{U}_C)$

electron gas interacting with screened Coulomb interaction

No screening in molecule





$$\Phi^{DC}[\rho^i_{local}] = \Phi^{H}[\rho^i_{local}] + \Phi^{X}[\rho^i_{local}] + \Phi^{LDA,C}[\rho^i_{local}]$$

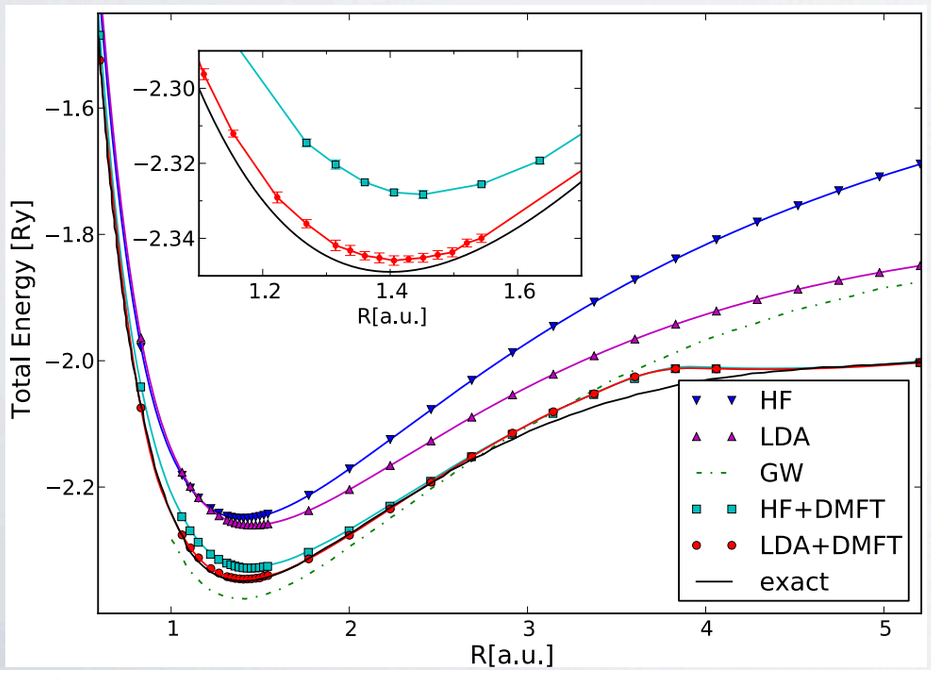
DMFT-like approximation for Hartree — *DMFT-like exchange* — *DMFT-like approximation for LDA correlations*

$$\Phi^{H}[\rho^i_{local}] = \frac{1}{2}\int_{\mathbf{r}\mathbf{r}'} \rho^i_{local}(\mathbf{r}) U_C(\mathbf{r}-\mathbf{r}')\rho^i_{local}(\mathbf{r}')$$

$$\Phi^{X}[\rho^i_{local}] = -\frac{1}{2}\sum_{\sigma}\int_{\mathbf{r}\mathbf{r}'} \rho^{\sigma,i}_{local}(\mathbf{r},\mathbf{r}') U_C(\mathbf{r}-\mathbf{r}')\rho^{\sigma,i}_{local}(\mathbf{r}',\mathbf{r})$$

bare Coulomb

$$\Phi^{LDA,C}[\rho^i_{local}] = \int_{\mathbf{r}} \varepsilon_c(\rho^i_{local}(\mathbf{r}))\rho^i_{local}(\mathbf{r}).$$



Juho Lee, KH, arXiv:1403.2474

Error of total energy using LDA+DMFT <0.2%!

IN SOLIDS HARDER | SCREENING

approximation: Yukawa form

$$\frac{1}{|\mathbf{r}-\mathbf{r}'|} \rightarrow \frac{e^{-\lambda|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|} \equiv U_{local}$$

Screening computed by GW or constrained RPA

DMFT approximation:

$$\Phi[\{G\}] \rightarrow^{DMFT} \rightarrow \Phi[\{G_{local}\}]$$

which means

$$G \rightarrow^{DMFT} \rightarrow G_{local}$$

$$\frac{1}{|\mathbf{r}-\mathbf{r}'|} \rightarrow^{DMFT} \rightarrow \frac{e^{-\lambda|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|}$$

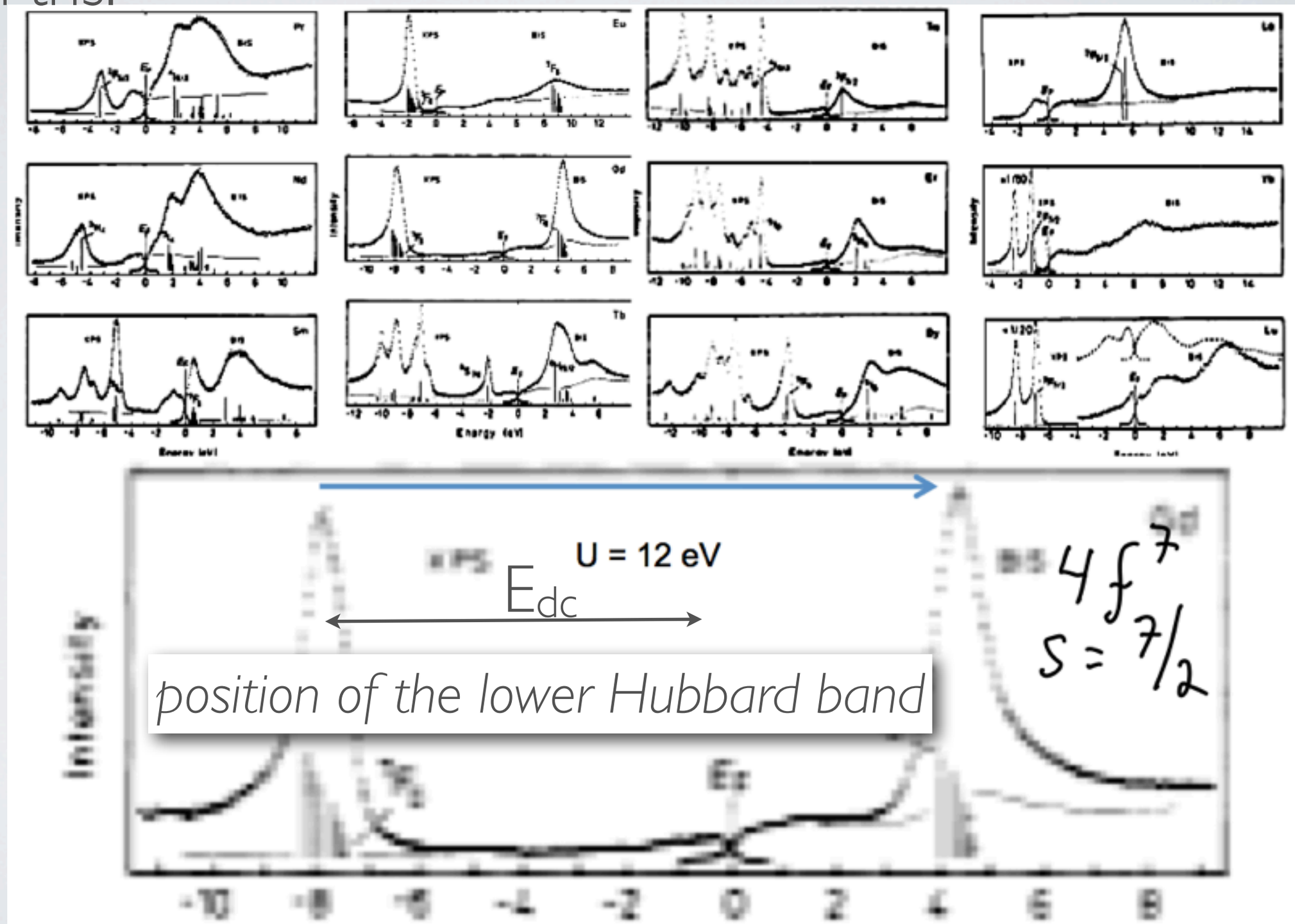
$$\Phi^{DC} = \sum_i \Phi^H_\lambda[\rho^i_{local}] + \Phi^{LDA,XC}_\lambda[\rho^i_{local}]$$

$$\Phi^{LDA,XC}_\lambda[\rho^i_{local}] = \int_{\mathbf{r}} \varepsilon_{xc}(\rho^i_{local}(\mathbf{r}), \frac{e^{-\lambda|\mathbf{R}|}}{|\mathbf{R}|})\rho^i_{local}(\mathbf{r})$$

This form of double-counting not yet implemented for solids

PHYSICS OF DC

Rare Earths:



position of the lower Hubbard band

WHAT IS COULOMB U?

Coulomb interaction between electrons:

$$\hat{U} = \frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\sum_{\sigma\sigma'}\psi^{\dagger}_{\sigma}(\mathbf{r})\psi^{\dagger}_{\sigma'}(\mathbf{r}')\frac{1}{|\mathbf{r}-\mathbf{r}'|}\psi_{\sigma'}(\mathbf{r}')\psi_{\sigma}(\mathbf{r})$$

Expansion of field operator $\psi_{\sigma}(\mathbf{r}) = \sum_{L}\phi_{L}(\mathbf{r})c_{L\sigma}$ where $\phi_{L}(\mathbf{r})$ set of functions

$$\hat{U} = \frac{1}{2}\sum_{L_1,L_2,L_3,L_4,\sigma,\sigma'} U_{L_1,L_2,L_3,L_4}c^{\dagger}_{L_1\sigma}c^{\dagger}_{L_2\sigma'}c_{L_3\sigma'}c_{L_4\sigma}$$

where $U_{L_1,L_2,L_3,L_4} = \int d\mathbf{r}d\mathbf{r}'\phi^{*}_{L_1}(\mathbf{r})\phi^{*}_{L_2}(\mathbf{r}')\frac{1}{|\mathbf{r}-\mathbf{r}'|}\phi_{L_3}(\mathbf{r}')\phi_{L_4}(\mathbf{r})$

Expansion in spherical harmonics: $\phi_{L}(\mathbf{r}) = R_{l}(r)Y_{L}(\hat{\mathbf{r}})$

Exact relation: $$\frac{1}{|\mathbf{r}-\mathbf{r}'|} = \sum_{k,m}\frac{4\pi}{2k+1}\frac{r^{k}_{<}}{r^{k+1}_{>}}Y_{km}(\hat{\mathbf{r}})Y^{*}_{km}(\hat{\mathbf{r}'})$$

Slater Form: $$U_{L_1,L_2,L_3,L_4} = \sum_{k}\frac{4\pi}{2k+1}\langle Y_{L_1}|\,Y_{km}\,|Y_{L4}\rangle\langle Y_{L_2}|\,Y^{*}_{km}\,|Y_{L3}\rangle F^{k}_{l_1,l_2,l_3,l_4}$$

Slater integrals: $$F^{k}_{l_1,l_2,l_3,l_4} = \int r^{2}dr\int r'^{2}dr'\frac{r^{k}_{<}}{r^{k+1}_{>}}R_{l_1}(r)R_{l_4}(r)R_{l_2}(r')R_{l_3}(r')$$

WHAT IS COULOMB U?

Slater Form: $$U_{L_1,L_2,L_3,L_4} = \sum_k \frac{4\pi}{2k+1} \langle Y_{L_1} | Y_{km} | Y_{L4} \rangle \langle Y_{L_2} | Y^*_{km} | Y_{L3} \rangle F^k_{l_1,l_2,l_3,l_4}$$

Special case $$l_1 = l_2 = l_3 = l_4$$

$$U_{m_1 m_2 m_3 m_4} = \sum_k \frac{4\pi}{2k+1} \langle Y_{lm_1} | Y_{k,m_1-m_4} | Y_{lm_4} \rangle \langle Y_{lm_2} | Y^*_{k,m_3-m_2} | Y_{lm_3} \rangle F^k_l$$

for l=0: $\langle \frac{1}{\sqrt{4\pi}} | Y_{k,m} | \frac{1}{\sqrt{4\pi}} \rangle = \delta_{k=0} \frac{1}{\sqrt{4\pi}}$ hence only k=0 is finite

for l=1: $\langle \begin{matrix} x \\ y \\ z \end{matrix} | Y_{k,m} | \begin{matrix} x \\ y \\ z \end{matrix} \rangle = \delta_{k=0} \ldots + \delta_{k=2} \ldots$ hence only k=0,2 is finite

for l=2: only k=0,2,4 is finite F^0, F^2, F^4

for l=3: only k=0,2,4,6 is finite F^0, F^2, F^4, F^6

ORDER OF MAGNITUDE

$$F_l^0 = 2\int_0^\infty r^2 dr R_l^2(r)\frac{1}{r}\int_0^r r'^2 dr' R_l^2(r') \approx \langle\frac{e^2}{r}\rangle$$

lets take: $r \approx r_B$ gives: $F_0 \approx 27.2eV$

lets take H 1s: $R(r) = \sqrt{\frac{4}{r_B^3}}e^{-r/r_B}$

$$F_l^2 = 2\int_0^\infty r^2 dr R_l^2(r)\frac{1}{r^3}\int_0^r r'^4 dr' R_l^2(r') \approx 0.26\langle\frac{e^2}{r}\rangle \approx 7.1\,eV$$

$$F_l^4 = 2\int_0^\infty r^2 dr R_l^2(r)\frac{1}{r^5}\int_0^r r'^6 dr' R_l^2(r') \approx 0.16\langle\frac{e^2}{r}\rangle \approx 4.4\,eV$$

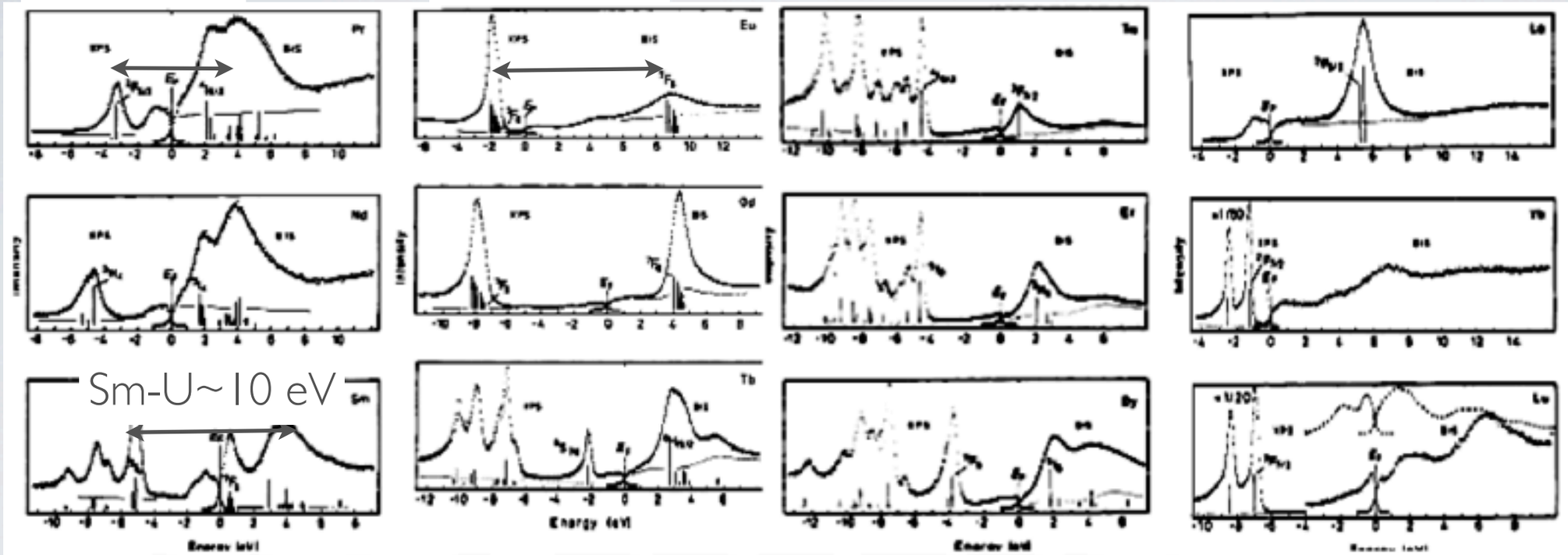
for d-shell we usually define: $F^2 = \frac{14}{1.625}J_H$ and $F^4 = \frac{14}{2.6}J_H$ hence $J_H \approx 0.82$

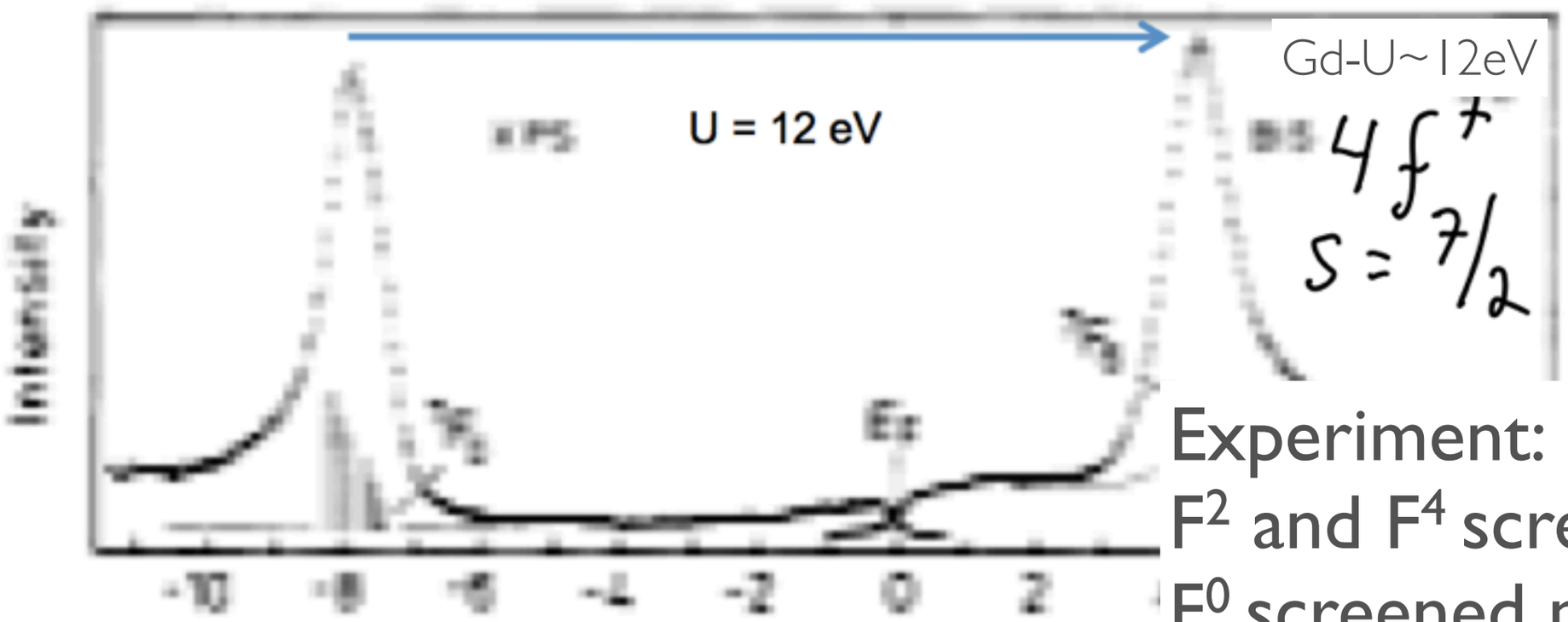
1) F^2 and F^4 are not small. Importance of Hunds coupling
2) F^0 is 2-4 times too large, J_H almost correct

Rare Earths: COULOMB U

Ce-U~6eV

Eu-U~11eV





Experiment:

F^2 and F^4 screened by 20%

F^0 screened much more

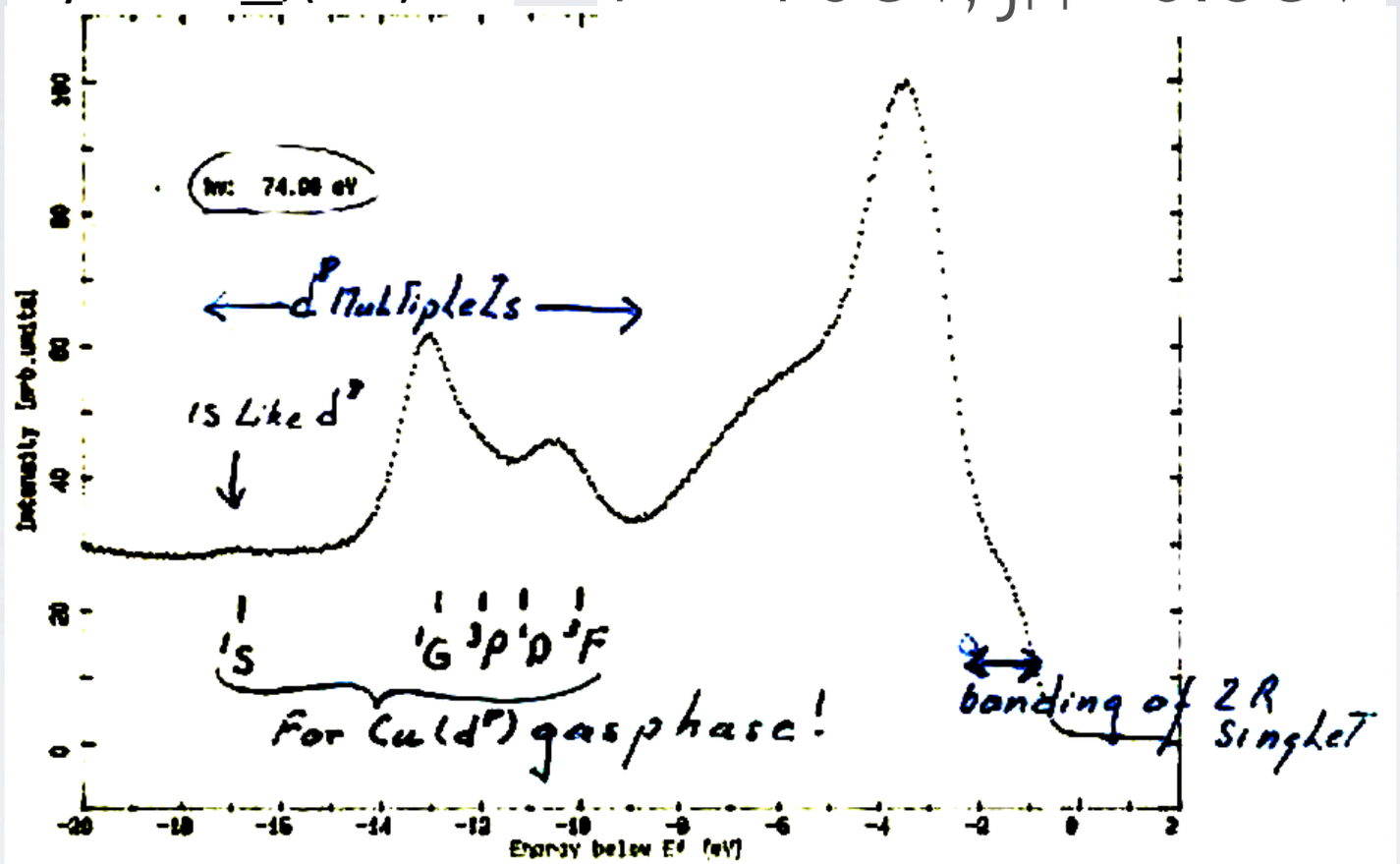
COULOMB U

Photoemission of CuO, Cu in d^9

J. Ghijsen et al

Phys. Rev. B. 42, (1990) 2268.

$F^0 = 10eV$, $J_H = 0.8eV$



Energy below Ef in eV

Exact diagonalization of the atom gives quite precise position of the peaks

REFRESH:HUNDS RULES

F2 and F4 ensure Hunds (1,2) rules:

1st) Maximize the total spin—spin parallel electrons must be in different spatial orbitals which reduces the Coulomb repulsion.

2nd)Rule then maximize the total orbital angular momentum L. This involves large m quantum numbers and lots of angular lobes and therefore electrons can avoid each other and lower Coulomb repulsion

3rd)< half filled shell J=L-S > half filled shell J=L+S (Result of spin orbit coupling)

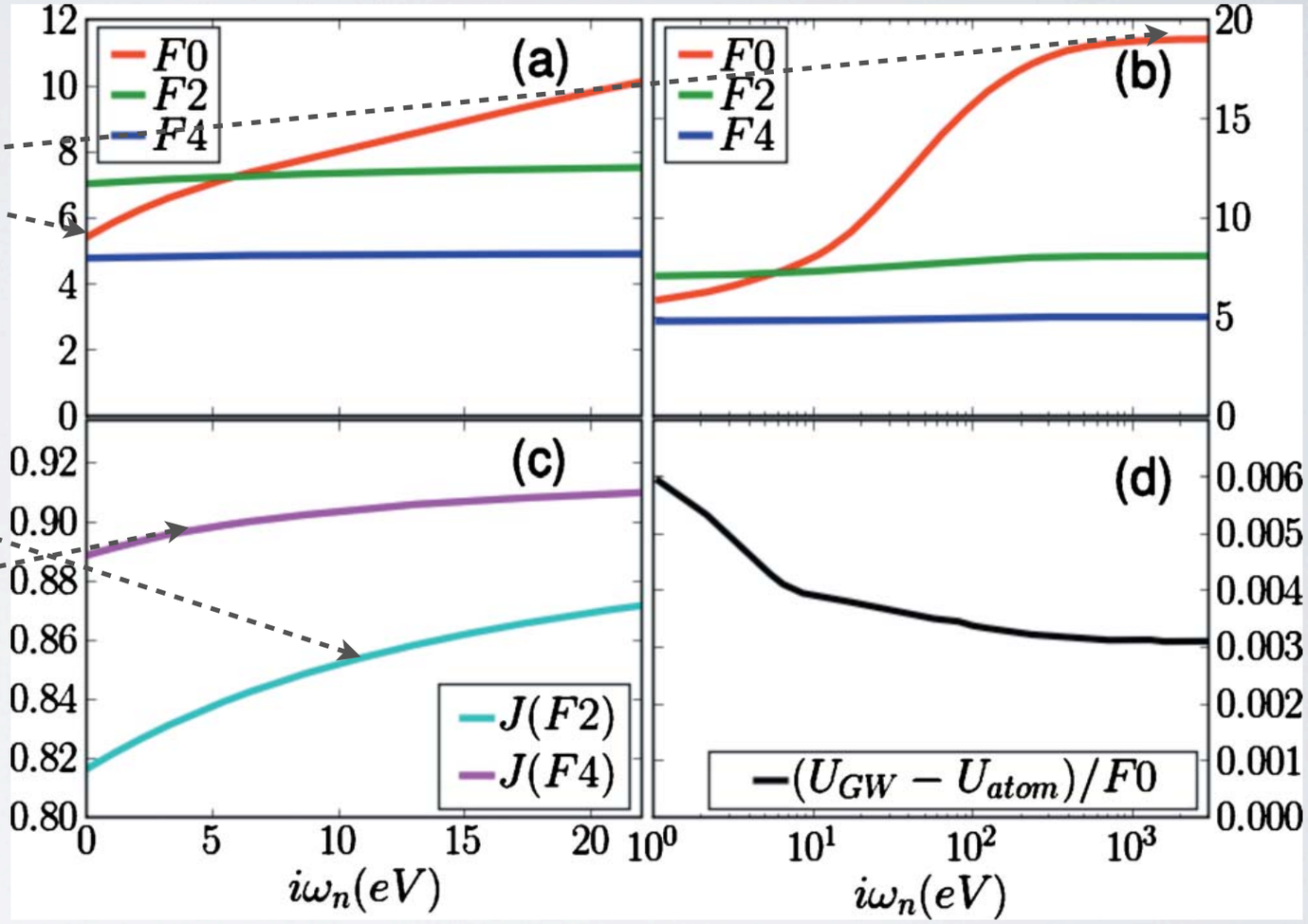
SCREENING OF COULOMB U IN FE-PNICTIDES

Kutepov, KH, S.Y. Savrasov, G. Kotliar, Phys. Rev. B 82, 045105 (2010)..

F_0 screened a lot from 20eV to 5eV

F_2 screened a bit

F_4 screened even less

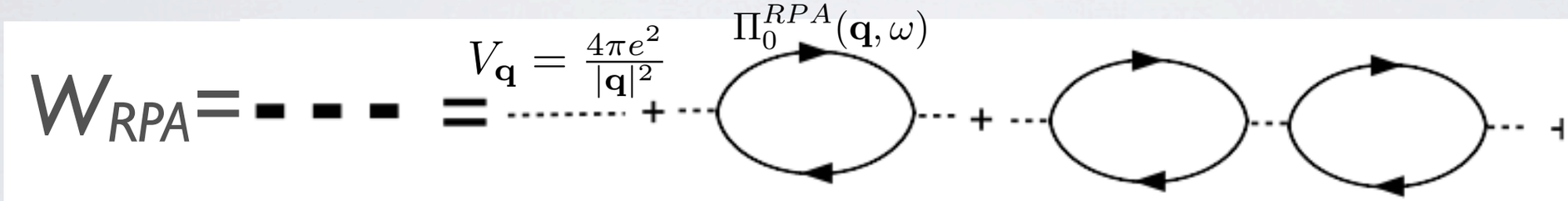


The method of choice:

- extended DMFT equations
- constrain RPA

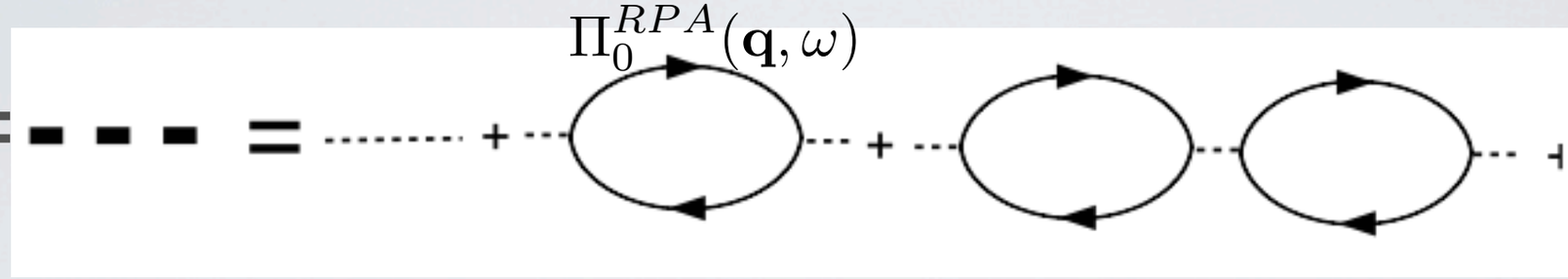
HOW TO COMPUTE SCREENING?

Within RPA world, the "fully screened" interaction ***W*** is the sum of bubbles:



$$W_{\mathbf{q}} = (V_{\mathbf{q}}^{-1} - \Pi_{\mathbf{q}})^{-1}$$

SIMPLEST CASE, SINGLE BAND

W_{RPA} = 

$$W_{\mathbf{q}} = \frac{1}{\frac{|\mathbf{q}|^2}{4\pi e_0^2} - \Pi_{\mathbf{q}}}$$

Lindhard formula:

$$\Pi_0^{RPA}(\mathbf{q},\omega) = \sum_{\mathbf{k}} \frac{f(\varepsilon_{\mathbf{k}}) - f(\varepsilon_{\mathbf{k+q}})}{\omega - \varepsilon_{\mathbf{k+q}} + \varepsilon_{\mathbf{k}}}$$

Low energy, long wavelength limit

$$\omega \to 0 \; \mathbf{q} \to 0$$

$$\Pi_0^{RPA}(\mathbf{q},\omega) = \sum_{\mathbf{k}} \frac{f(\varepsilon_{\mathbf{k}}) - f(\varepsilon_{\mathbf{k+q}})}{\varepsilon_{\mathbf{k}} - \varepsilon_{\mathbf{k+q}}} = \sum_{\mathbf{k}} \left(\frac{\partial f}{\partial \varepsilon_{\mathbf{k}}} \right) = -D(\omega = 0)$$

Interaction screened by Yukawa form

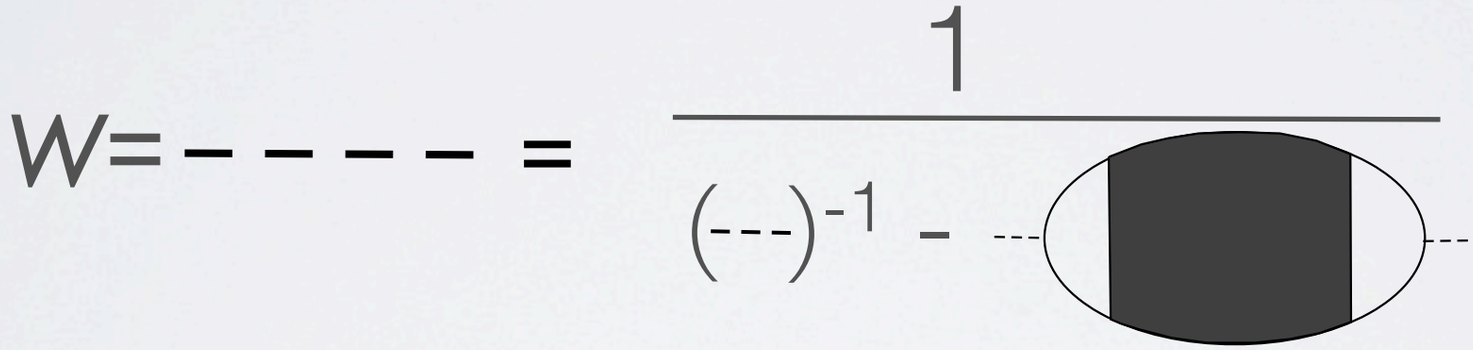
$$W_{\mathbf{q}\to 0} = \frac{4\pi e_0^2}{|\mathbf{q}|^2 + 4\pi e_0^2 D(0)}$$

$$W(\mathbf{r}\mathbf{r}') \approx \frac{e^{-\sqrt{4\pi e_0^2 D(0)}|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|}$$

HOW TO COMPUTE SCREENING?

$$W_{\mathbf{q}} = (V_{\mathbf{q}}^{-1} - \Pi_{\mathbf{q}})^{-1}$$

In exact theory, the "fully screened" interaction is vertex corrected:



$\Pi_{\mathbf{q}}$ in general different from $\Pi^0_{\mathbf{q}}$

However, U is not the "fully screened" interaction!
U is screened by the degrees of freedom not taken into account by DMFT!

SCREENING OF COULOMB U

Important: Only screening processes excluded in DMFT screen U!

Thought experiment:

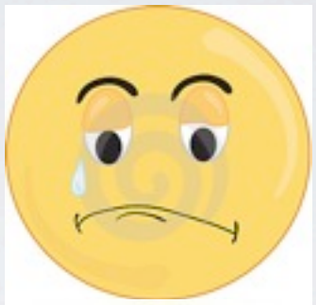
Imagine we know the exact "fully screened interaction" ***W***. We also solve the problem by DFT+DMFT at chosen U. We compute ***W*** within DFT+DMFT and when ***W*** within DFT+DMFT matches the exact ***W*** (projected on DMFT degrees of freedom) we found correct U.

$$W^{DMFT} = (U^{-1} - \Pi_{DMFT})^{-1} = P \otimes P \, W^{exact}$$

SCREENING OF COULOMB U

Kutepov, KH, S.Y. Savrasov, G. Kotliar, Phys. Rev. B 82, 045105 (2010)..

We do not know exact ***W***!



Let's use RPA instead.

We solve the band structure problem with RPA
(actually called GW)!
We also solve the DMFT problem with RPA (not with DMFT)

$$W^{model-RPA} = (U^{-1} - \Pi^{model-RPA})^{-1} = P \otimes P\, W^{GW}$$

with $\Pi^{model-RPA} = G_{local} * G_{local}$

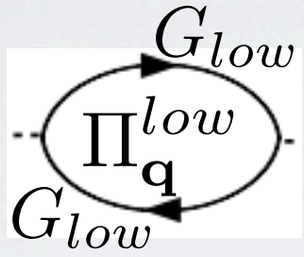
CONSTRAINED RPA

F. Aryasetiawan et.al., PRB **70**, 195104 (2004)

Similar idea but cutting in space of bands, instead of projectors

$$\Pi_{\mathbf{q}} = \Pi^{rest}_{\mathbf{q}} + \Pi^{low}_{\mathbf{q}}$$

$$V_{\mathbf{q}} = \frac{4\pi e^2}{|\mathbf{q}|^2}$$



$$W_{\mathbf{q}} = \frac{1}{V^{-1}_{\mathbf{q}} - \Pi^{rest}_{\mathbf{q}} - \Pi^{low}_{\mathbf{q}}}$$

$$W^{low}_{\mathbf{q}} = \frac{1}{U^{-1} - \Pi^{low}_{\mathbf{q}}}$$

$$U^{-1} = V^{-1}_{\mathbf{q}} - \Pi^{rest}_{\mathbf{q}}$$

rest: high energy bands U=0

EF — low-E bands — U≠0

rest: high energy bands U=0

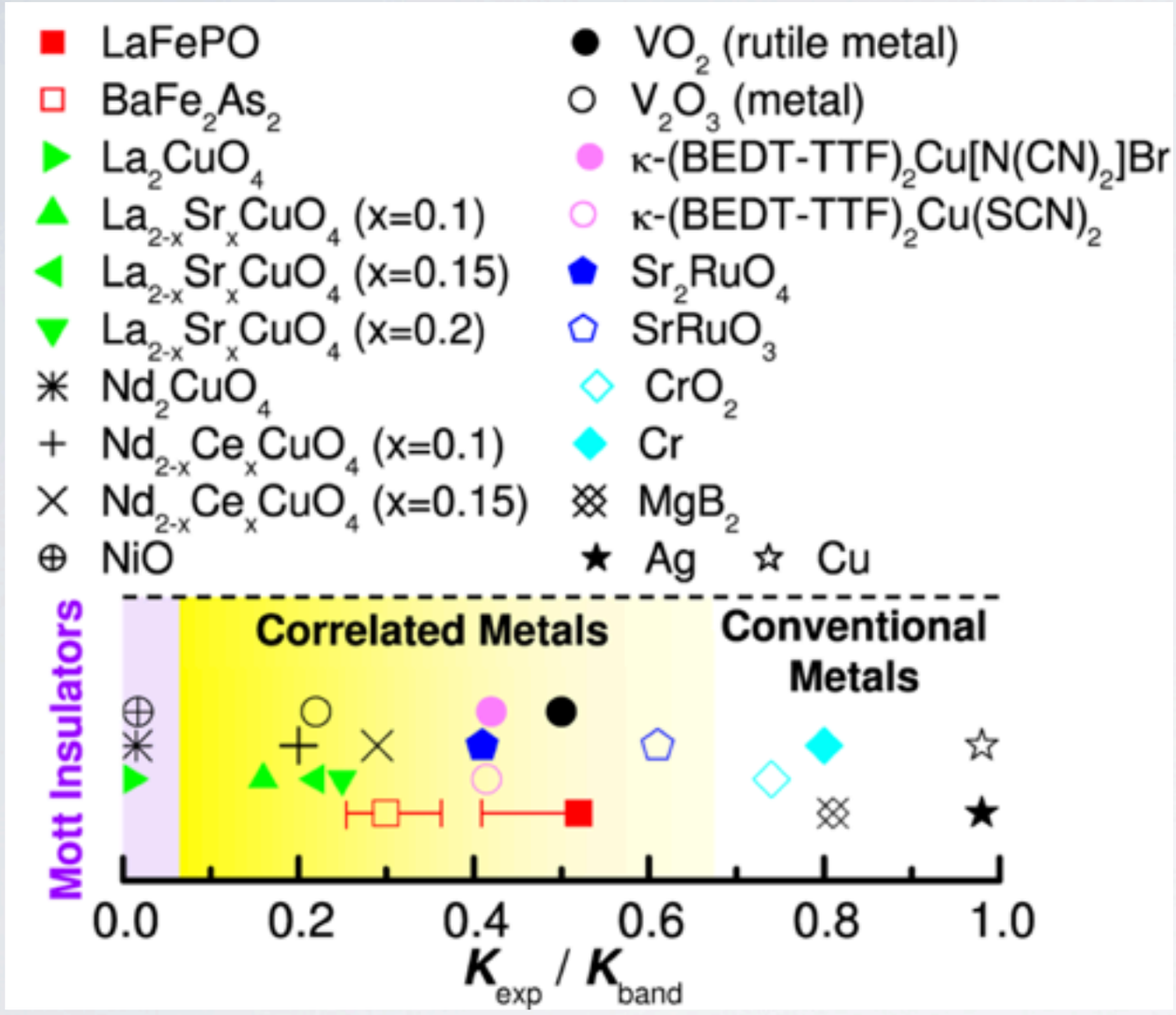
Good for Hubbard model U.

Not good for all electron DFT+DMFT: "rest" states that have no explicit U in DMFT, but interact through DFT by Hartree and XC functional and screen W.

In materials with entangled bands, it leads to ridiculous small U's

Cerium alpha phase U<0.5eV.

IMPORTANCE OF HUNDS COUPLING



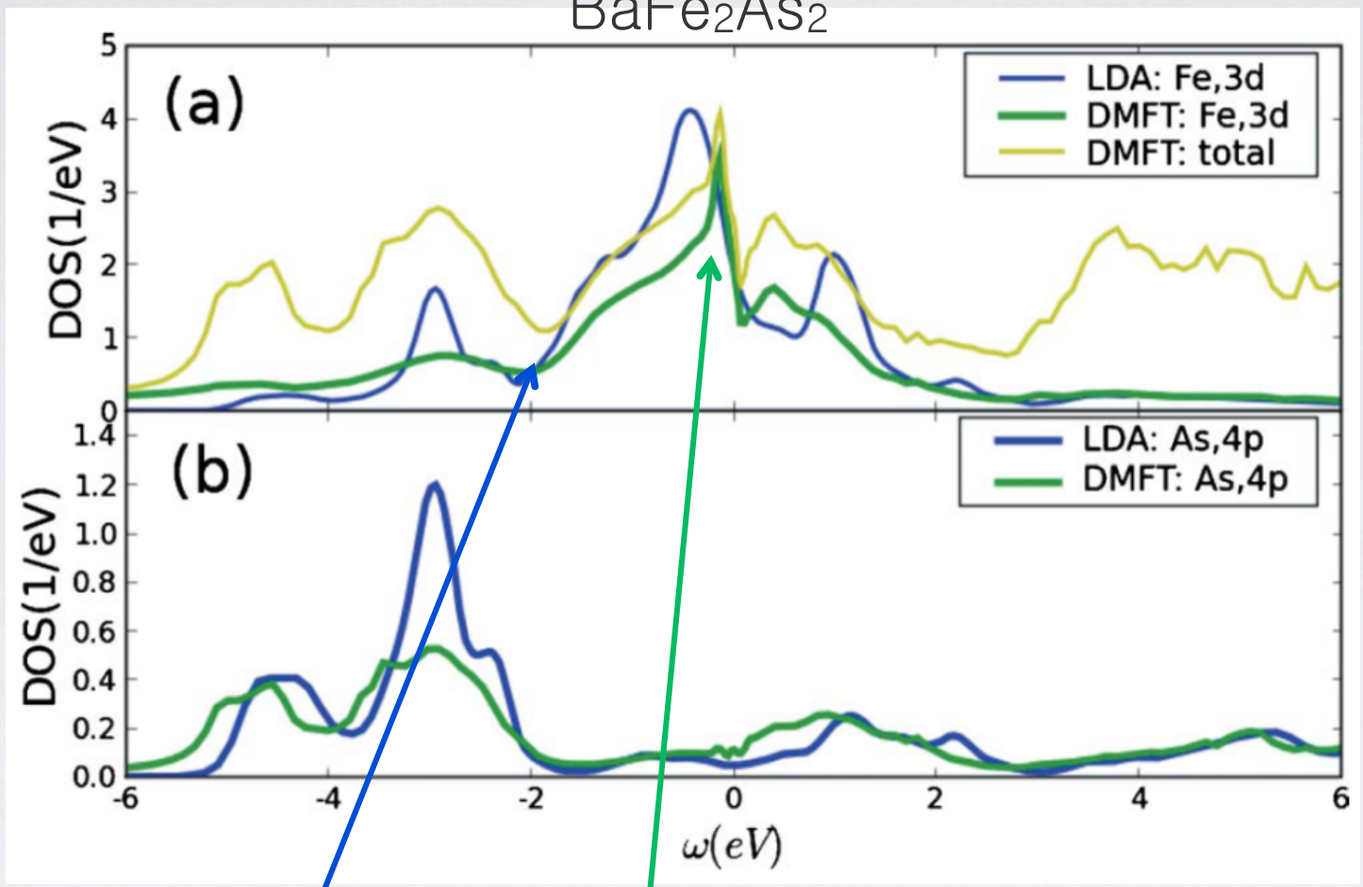
Most of theorists at the beginning of iron era (2008) were proposing weak correlations in pnictides

mass enhancements of optimally doped cuprates and iron pnictides very similar.

Why?

D. Basov, R. Averitt, D. van der Marel, M. Dressel, KH, RMP, 83, 471 (2011)

One particle spectra of Hunds metals (pnictides)



Renormalized q.p. peak

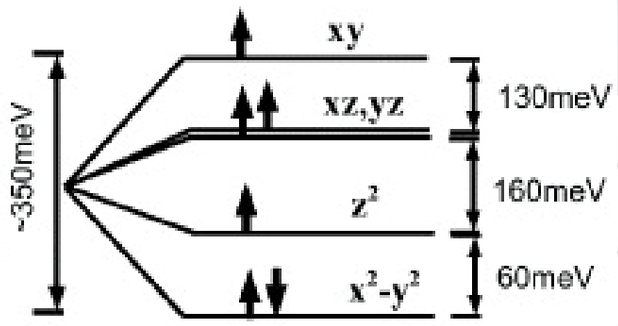
High energy not very different from LDA

No clear Hubbard band in one particle spectra
Many theorists took this is a sign of weak correlation strength

Importance of Hund's rule in pnictides: **Hunds Metals**

Significant Correlations in pnictides: effective mass 3-5 band mass

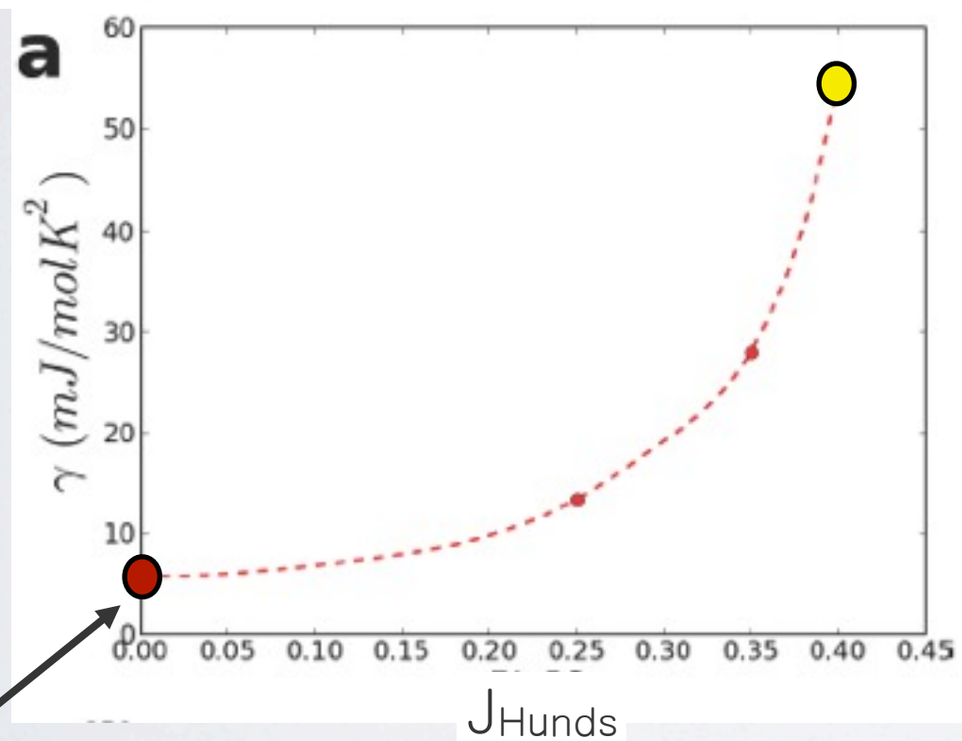
KH, J.H. Shim, and G. Kotliar, PRL 100, 226402 (2008)



Hubbard U not important

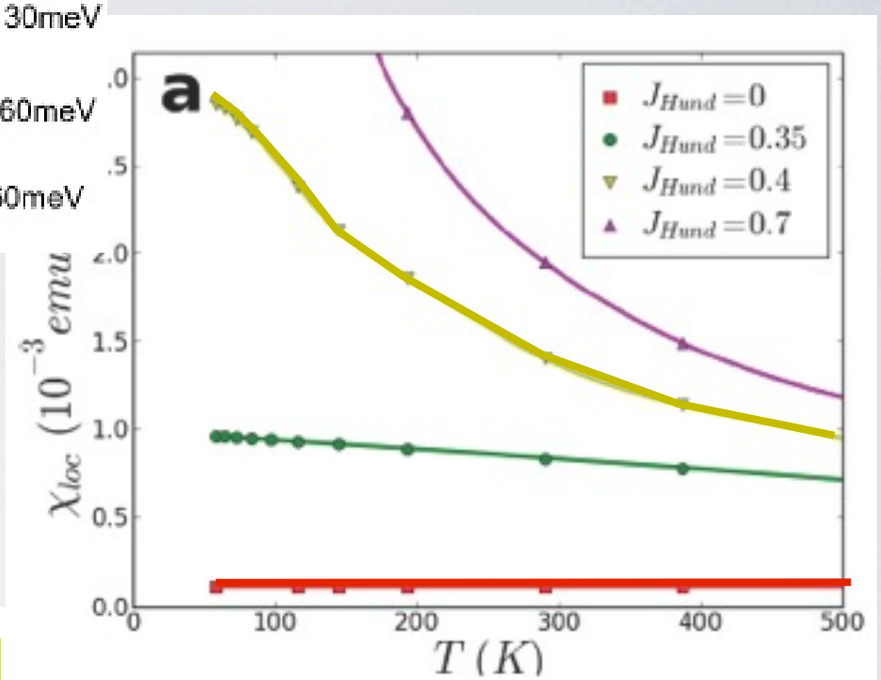
The **Hund's coupling** brings correlations!

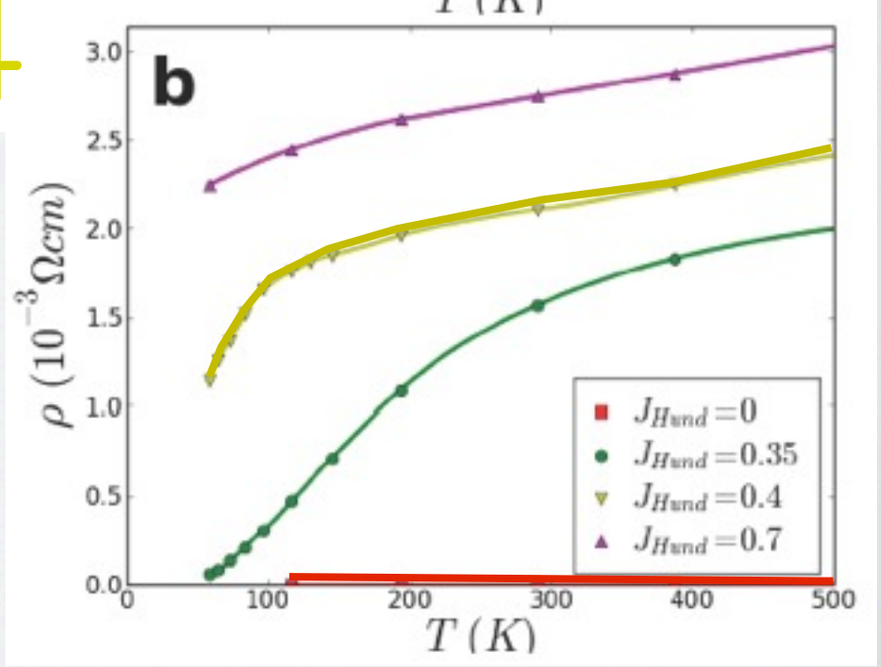
KH, G. Kotliar, arXiv:0805.0722 (2008)
New Journal of Physics, 11 025021 (2009).



U=4eV

J=0.4





LDA value

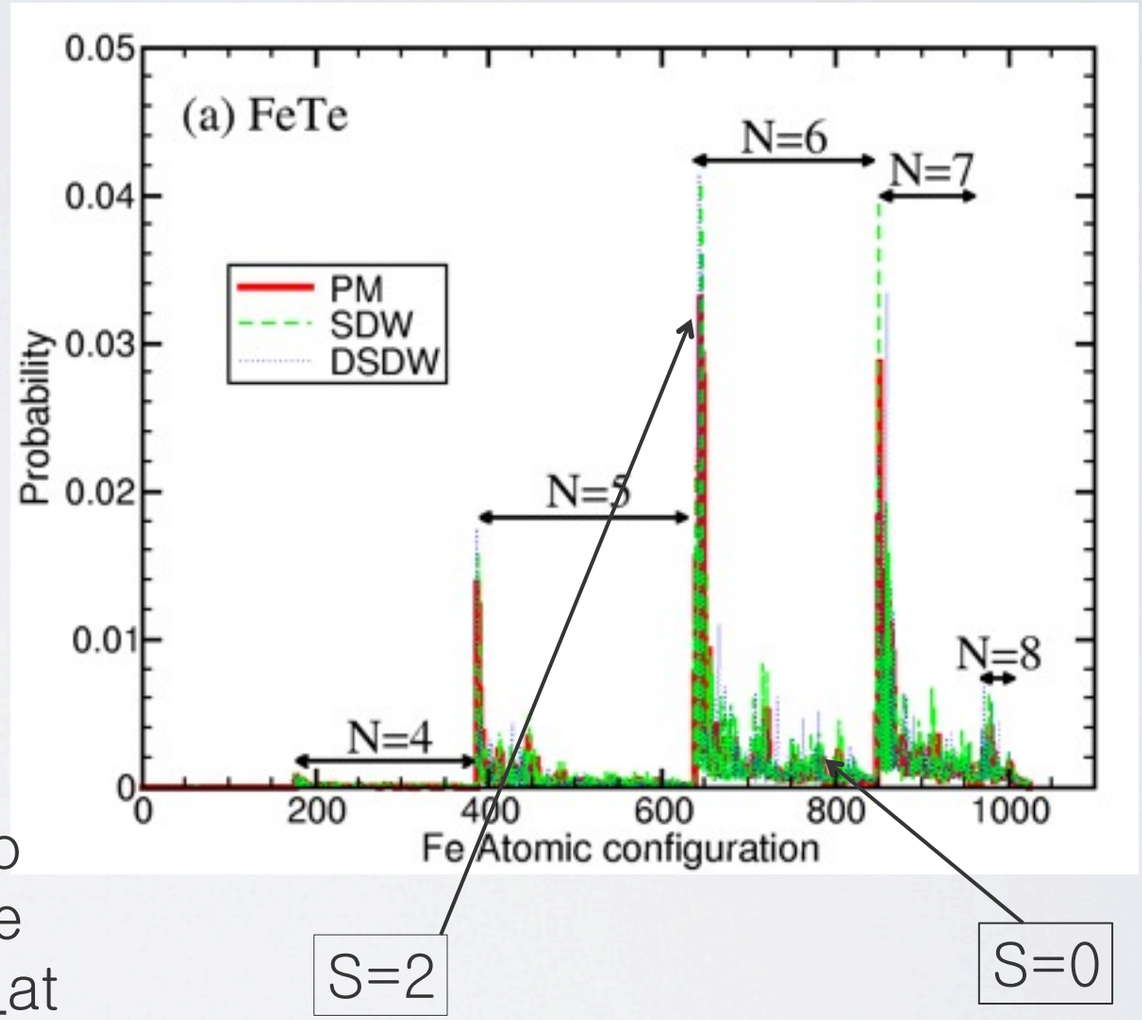
For J=0 there is negligible mass enhancement at U~W!

Histogram of Hunds metals

In oxydes, only a few atomic states (one in each valence) with significant Probability

In pnictides, many states with large probability -> charge fluctuations are not efficiently blocked by Coulomb U. (more itinerant system)

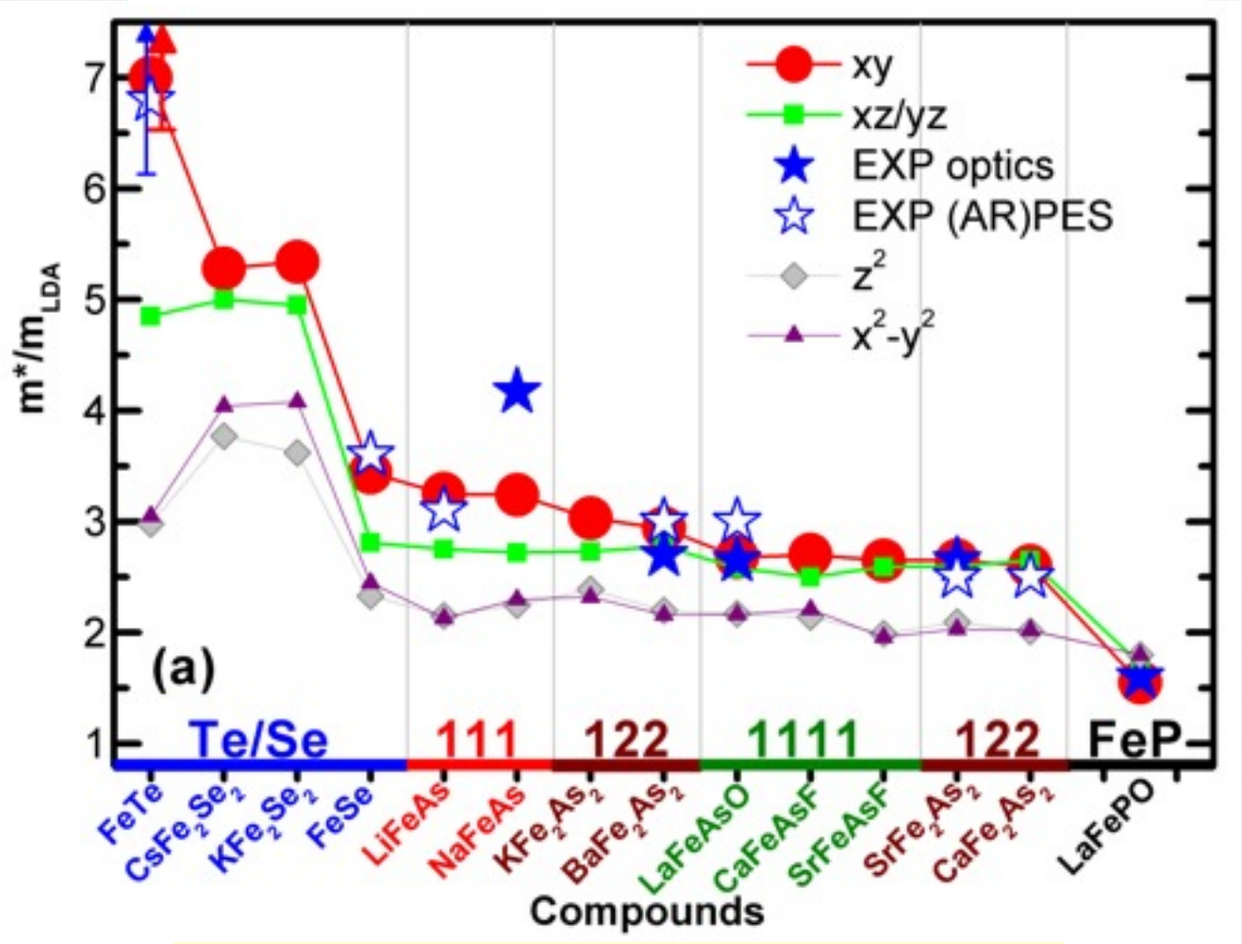
States with high spin more probable than those with low spin -> gives rise to non-Fermi liquid physics at intermediate temperatures, and heavy quasiparticles at Low temperatures.



Mass enhancement & Magnetic moment

Z. P.Yin, KH, G. Kotliar, Nature Materials (2011)

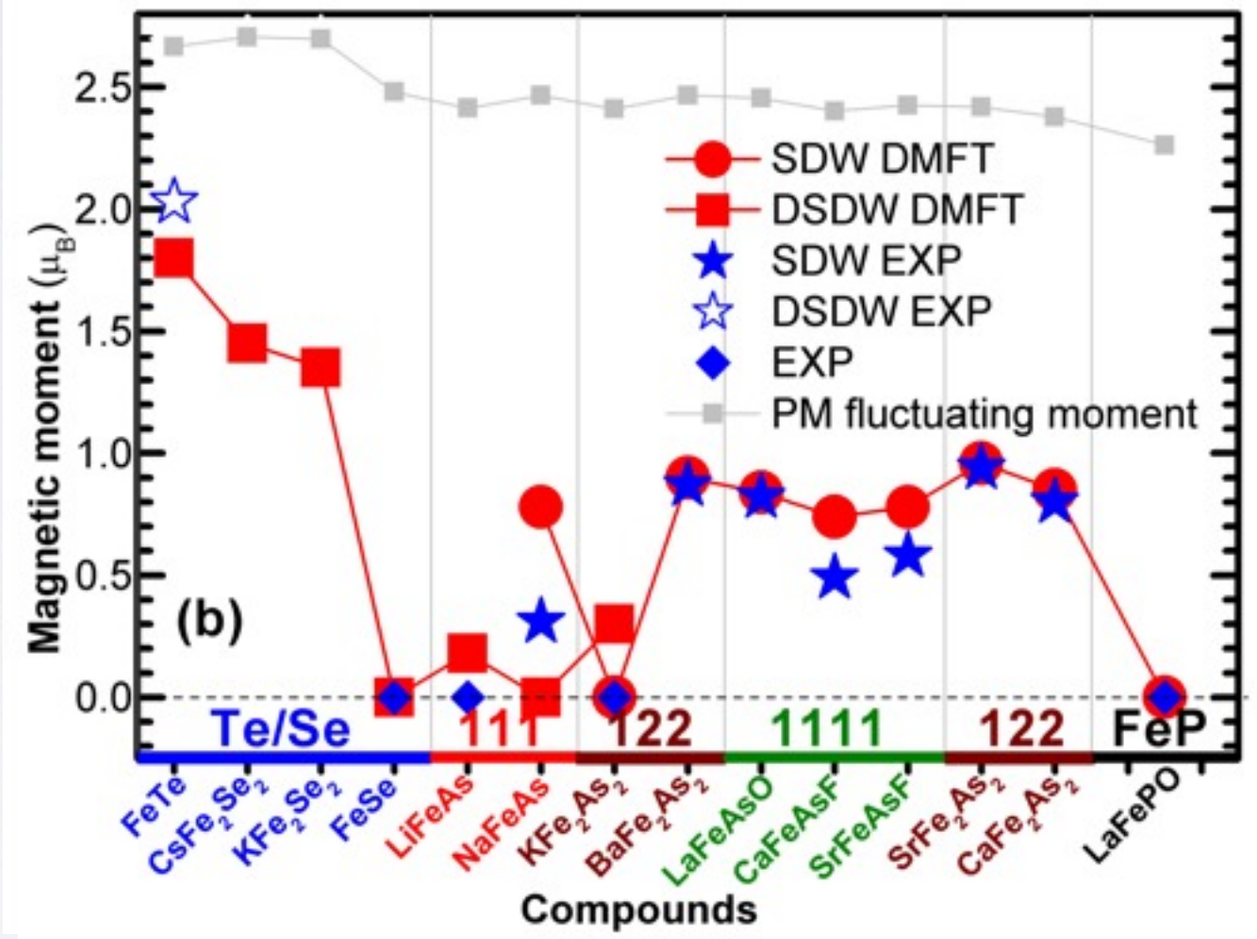
Correlation diagram of Hund's metals



Mass enhancement substantial
Electrons have dual nature

Good agreement with experiment!(fixed U=5eV, J=0.8eV determined by first principles PRB 82, 045105 (2010)).

Static ordered moment within LDA+DMFT



Static ordered moment very small

moment<->mass
Some similarity, but also many differences!

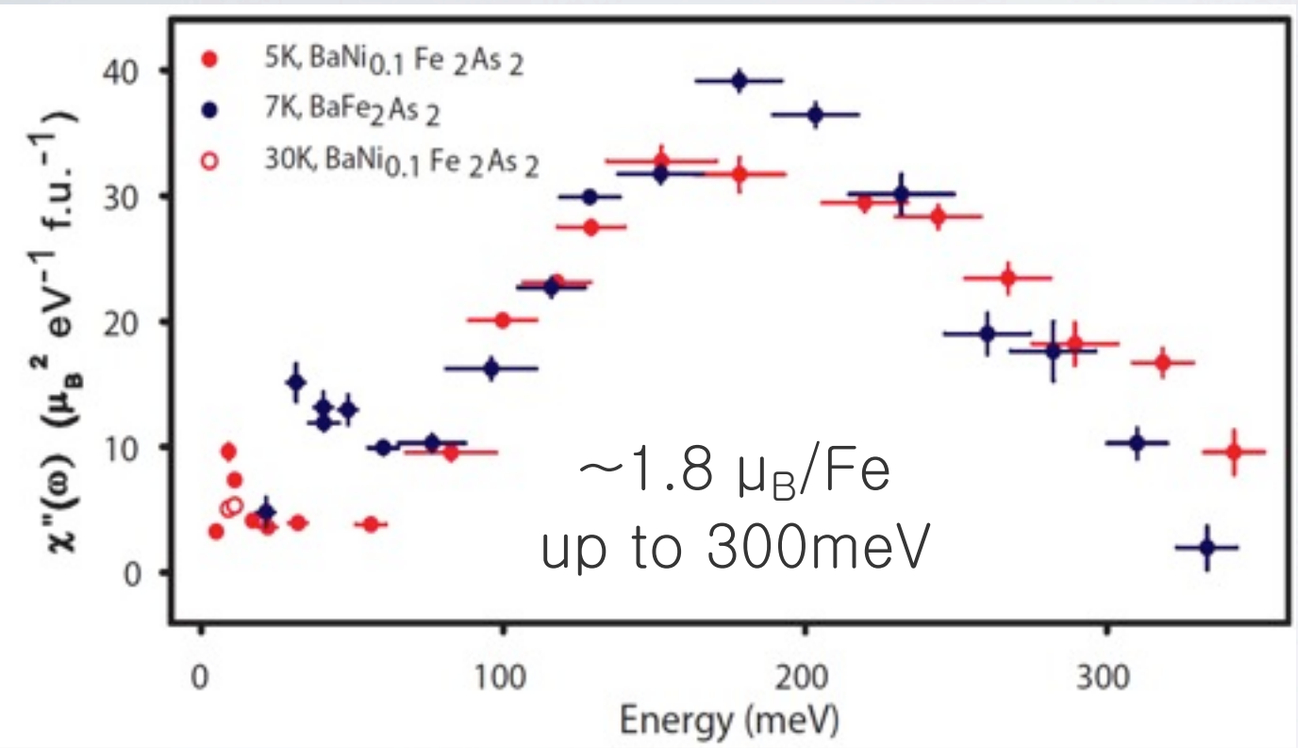
NO FITTING PARAMETER

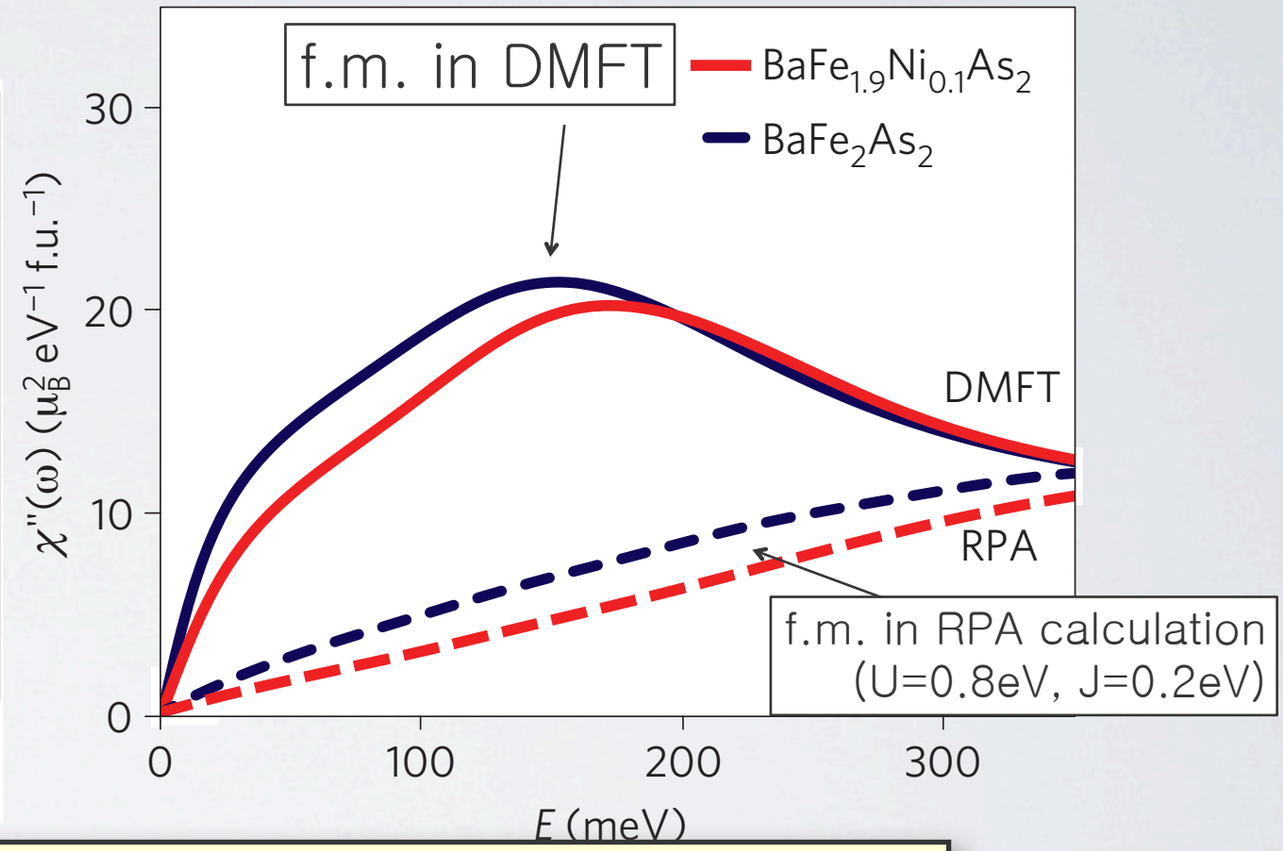
Large fluctuating moment

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

M. Liu, et.al., Nature Physics 8, 376-381 (2012)

Experiment by Pengcheng Dai



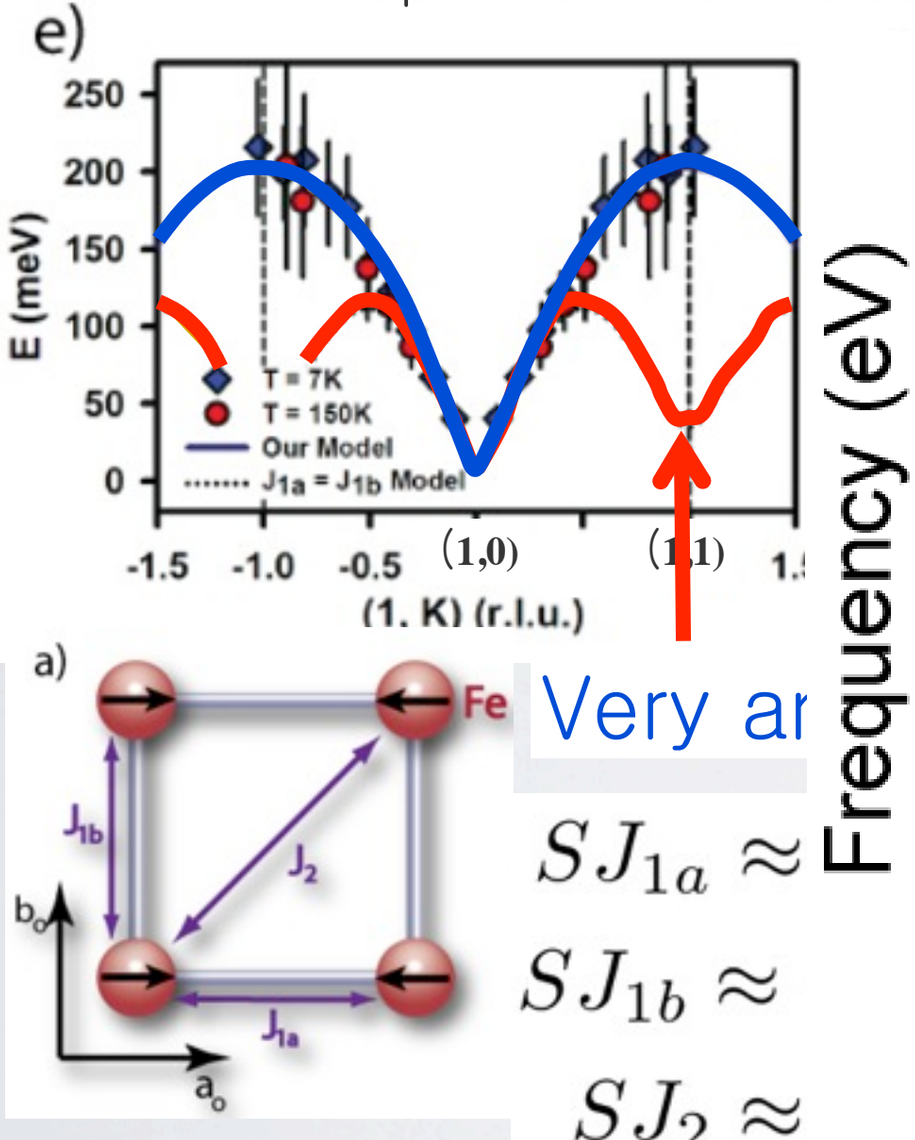


Large fluctuating moment can not be explained by a purely itinerant model - property of Hundsness!

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

Dynamical structure factor of $BaFe_2As_2$

Spin wave for Heissenberg model

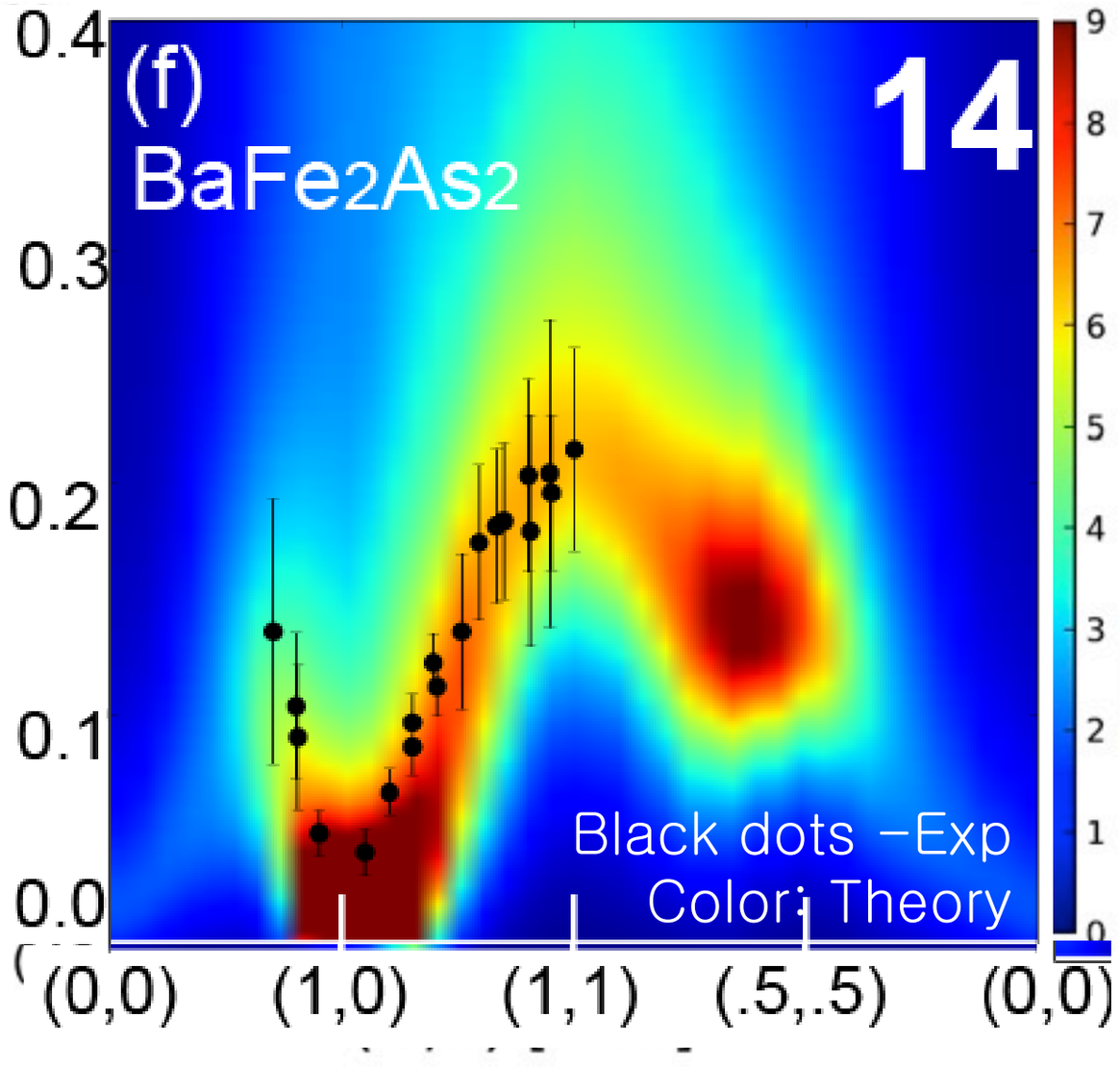


Very ar

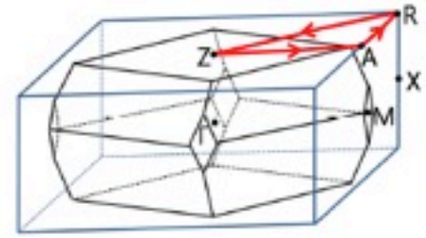
$$SJ_{1a} \approx$$

$$SJ_{1b} \approx$$

$$SJ_2 \approx$$



DMFT



Leland W. Harriger, Pengcheng Dai et al., PRB 84, 054544 (2011).

S(q,**ω**) in paramagnetic phase similar to AFM phase!
No anysotropy needed (above T_S) to explain neutrons.

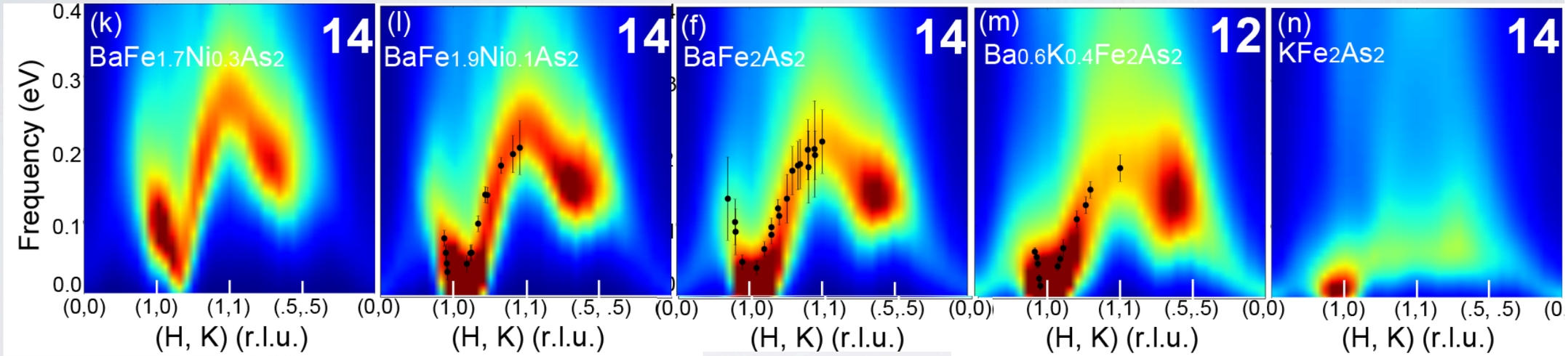
Theoretical Magnetic excitations

Doping variation

Z.P. Yin, K. Haule, G. Kotliar,
arXiv 1311.1188

electron doping ⟵ hole doping ⟶

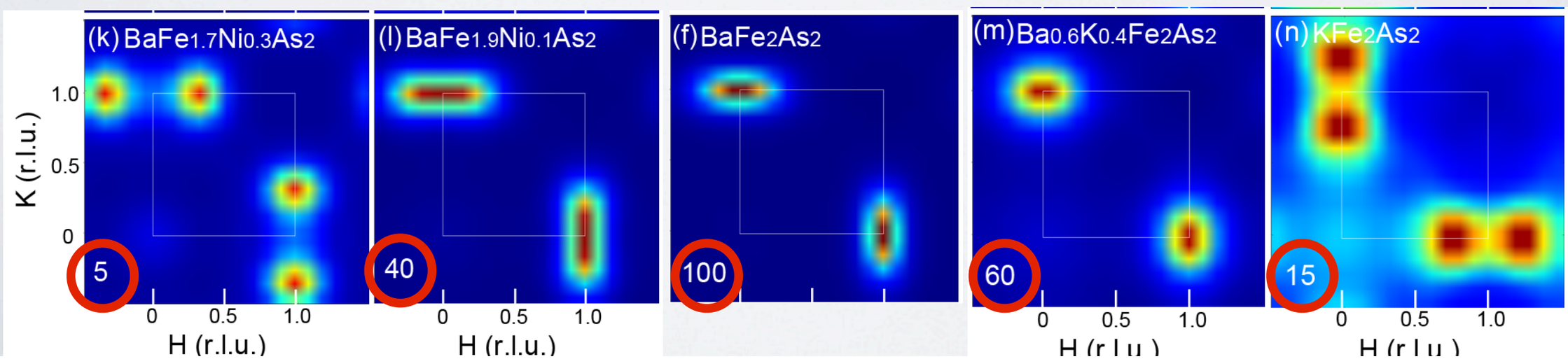
$T_C < 2K$ $T_C = 20K$ *AFM* $T_C = 39K$ $T_C = 3.5K$



electron overdoped:
low energy spin excitations
very weak
and become **incommensurate**

Optimally doped:
Commensurate low energy
strong low energy
strong high energy

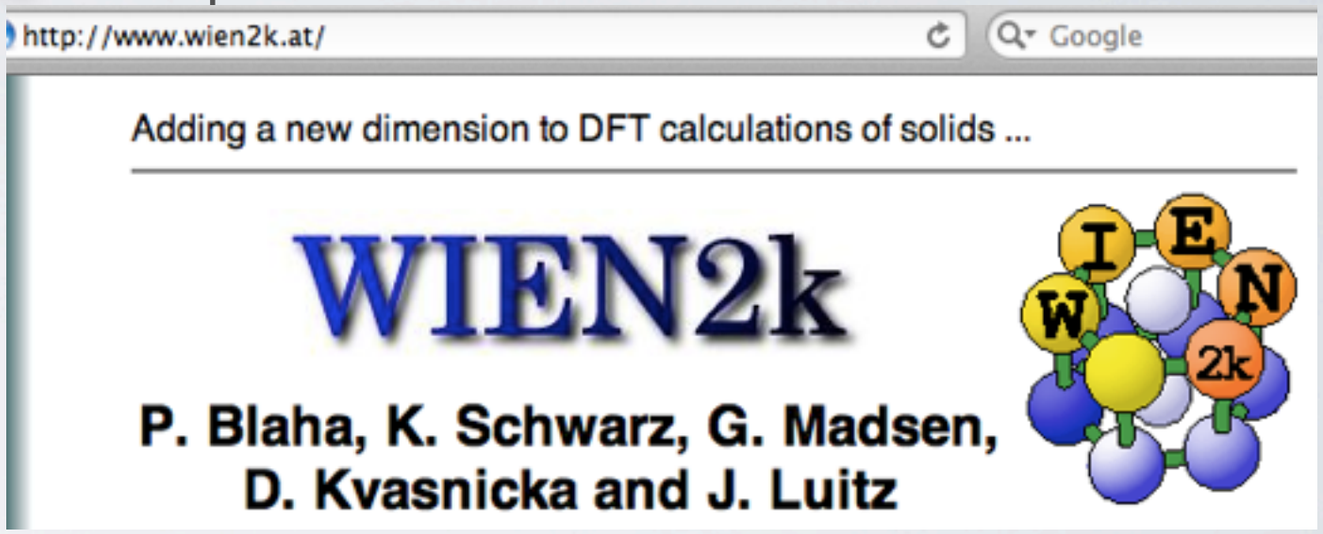
hole overdoped:
low energy spin excitations
weaker
and **incommensurate**



IMPLEMENTATION

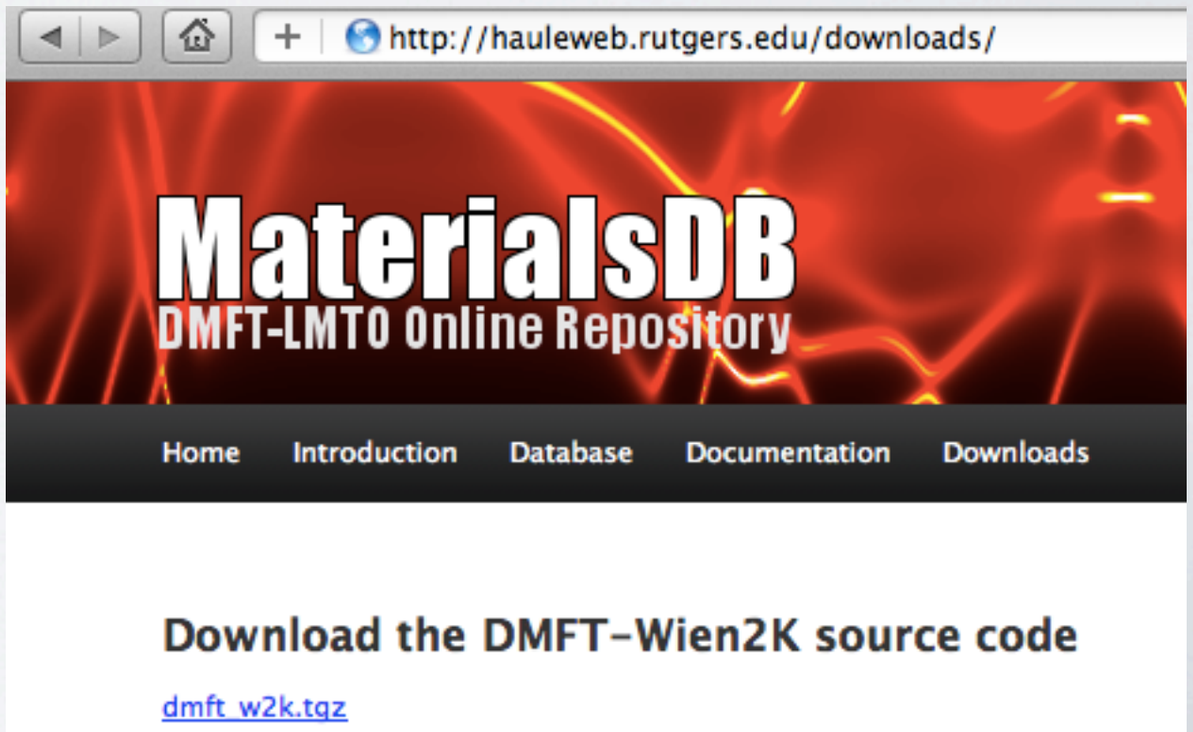
DFT code based on Wien2K: http://www.wien2k.at/

nice manual:
http://www.wien2k.at/reg_user/textbooks/usersguide.pdf



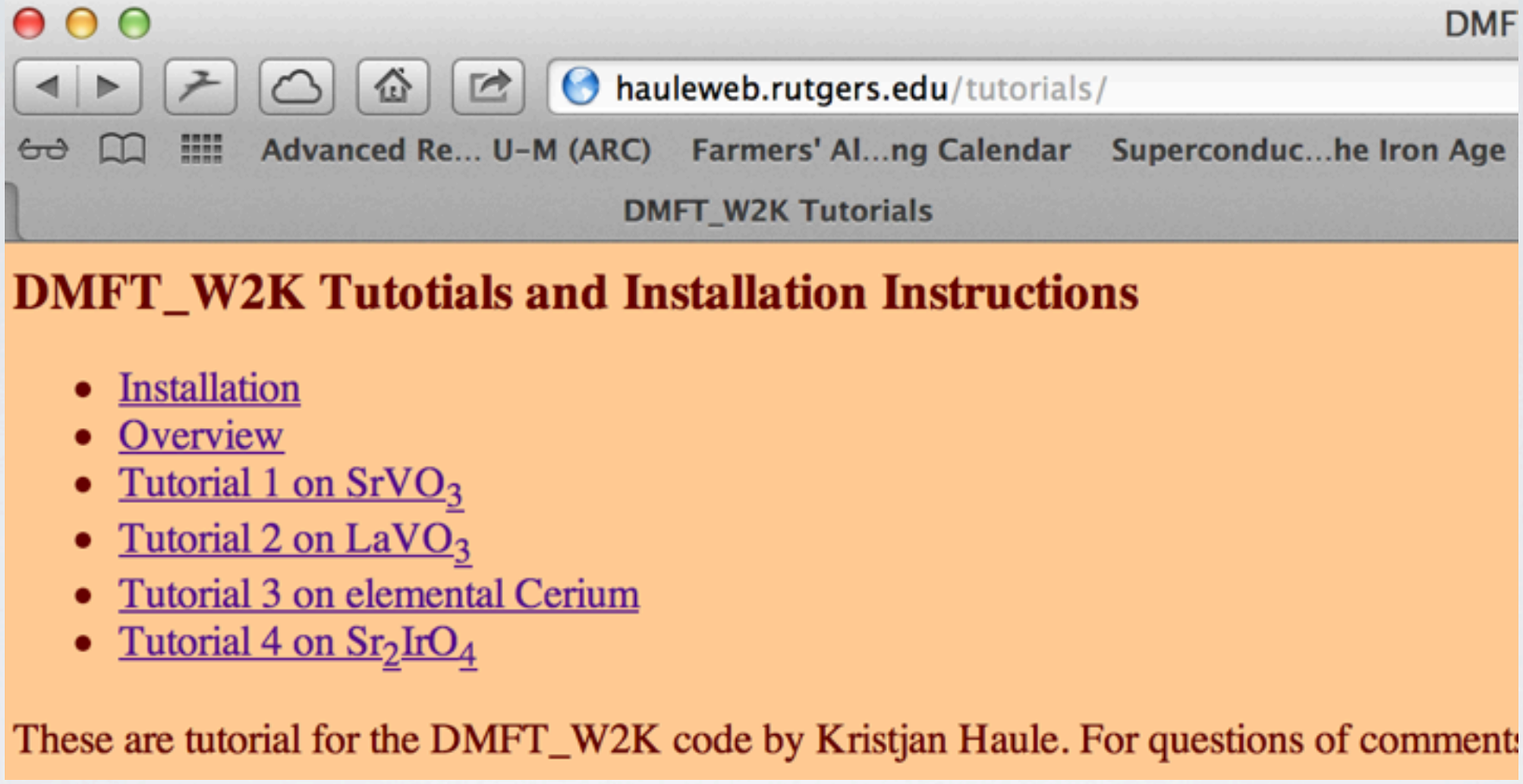
DMFT part and interface developed at Rutgers:

http://hauleweb.rutgers.edu/



TUTORIALS

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



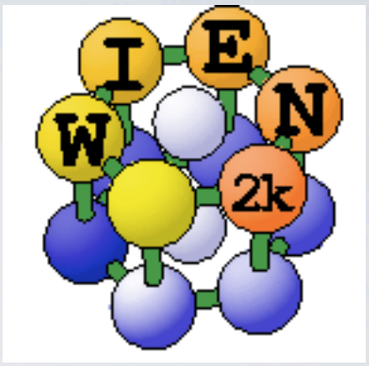
Several tutorials to get you familiar with the code.
Starts with very simple cubic system, to Mott insulator that requires rotated local basis (LaVO3) to most sophisticated 5d system which requires rotation and local transformation to J=1/2-like states.

DFT PART

init_lapw : $\rho^{atom}(\mathbf{r})$

run_lapw ==

x lapw0 : $V_{ext}(\mathbf{r})\ \rho(\mathbf{r}) \rightarrow V_{KS}(\mathbf{r})$



x mixer: $\rho^{val} + \rho^{core}, \rho^{old}(\mathbf{r}) \rightarrow \rho^{new}(\mathbf{r})$

x lapw1 : $V_{KS}(\mathbf{r}), V_{ext}(\mathbf{r}) \rightarrow \varepsilon^{DFT}_{\mathbf{k},i}, \psi^{DFT}_{\mathbf{k},i}$

x core : $V_{KS}(\mathbf{r}), V_{ext}(\mathbf{r}) \rightarrow \rho_{core}(\mathbf{r}), E_{core}$

x lapwso : *adds spin-orbit*

x lapw2: $\varepsilon^{DFT}_{\mathbf{k},i}, \psi^{DFT}_{\mathbf{k},i} \rightarrow \rho^{val}(\mathbf{r}), E_{valence}$

DFT+DMFT COMBINED

run_lapw : $\rho^{DFT}(\mathbf{r})$

run_dmft.py ==

x lapw0 : $V_{ext}(\mathbf{r})\ \rho(\mathbf{r}) \rightarrow V_{KS}(\mathbf{r})$

x mixer: $\rho^{val} + \rho^{core}, \rho^{old}(\mathbf{r}) \rightarrow \rho^{new}(\mathbf{r})$

x lapw1 : $V_{KS}(\mathbf{r}), V_{ext}(\mathbf{r}) \rightarrow \varepsilon^{DFT}_{\mathbf{k},i}, \psi^{DFT}_{\mathbf{k},i}$

x core : $V_{KS}(\mathbf{r}), V_{ext}(\mathbf{r}) \rightarrow \rho_{core}(\mathbf{r}), E_{core}$

x lapwso : *adds spin-orbit*

x_dmft.py dmft2 :
$\Sigma^{DMFT}(\omega), \varepsilon^{DFT}_{\mathbf{k},i}, \psi^{DFT}_{\mathbf{k},i} \rightarrow \rho^{val}(\mathbf{r}), E_{valence}$

x_dmft.py dmft1 :
$\Sigma^{DMFT}(\omega), \varepsilon^{DFT}_{\mathbf{k},i}, \psi^{DFT}_{\mathbf{k},i} \rightarrow G^{DMFT}(\mathbf{r}), \Delta(\omega)$

impurity solver: CTQMC,OCA,NCA
$\Delta(\omega), E_{imp} \rightarrow \Sigma(\omega), G^{DMFT}$

dmft1 step

input → output

$$\Sigma(\omega), \varepsilon^{DFT}_{\mathbf{k},i}, \psi^{DFT}_{\mathbf{k},i} \rightarrow G_{local}, \Delta(\omega), E_{imp}$$

1) Constructs projector: $P(\mathbf{r}\mathbf{r}', \tau L L') \approx Y_L(\hat{\mathbf{r}}_\tau)\delta(r_\tau - r'_\tau)Y^*_{L'}(\hat{\mathbf{r}}'_\tau)$

2) Embeds self-energy: $\overline{\Sigma}_{\mathbf{k},ij}(\omega) = \sum_{\tau, L_1 L_2} P_{\mathbf{k}\tau}(ji, \tau L_2 L_1)(\Sigma^\tau_{L_1 L_2}(\omega) - E^\tau_{dc})$

3) Calculates local Green's function and hybridization function

$$G_{local}{}^\tau_{LL'} = \sum_{\mathbf{k}ij} P_{\mathbf{k}\tau}(ij, LL') \left[\left(i\omega + \mu - \epsilon_{\mathbf{k}} - \overline{\Sigma}_{\mathbf{k}}(\omega) \right)^{-1} \right]_{ji}$$

$$= \left[\frac{1}{i\omega - E^\tau_{imp} - \Sigma^\tau(\omega) - \Delta^\tau(\omega)} \right]_{LL'}$$

dmft2 step

input → output

$$\Sigma(\omega), \varepsilon^{DFT}_{\mathbf{k},i}, \psi^{DFT}_{\mathbf{k},i} \rightarrow \rho^{DMFT}_{val}(\mathbf{r}), E_{valence}$$

1) Constructs projector: $P(\mathbf{r}\mathbf{r}', \tau L L') \approx Y_L(\hat{\mathbf{r}}_\tau)\delta(r_\tau - r'_\tau)Y^*_{L'}(\hat{\mathbf{r}}'_\tau)$

2) Embeds self-energy: $\overline{\Sigma}_{\mathbf{k},ij}(\omega) = \sum_{\tau, L_1 L_2} P_{\mathbf{k}\tau}(ji, \tau L_2 L_1)(\Sigma^\tau_{L_1 L_2}(\omega) - E^\tau_{dc})$

3) Solves Dyson Eq.: $\left(-\nabla^2 + V_{KS}(\mathbf{r}) + \overline{\Sigma}_{\mathbf{k}}(\omega)\right)\psi_{\mathbf{k}\omega_n i}(\mathbf{r}) = \varepsilon^{DMFT}_{\mathbf{k}\omega_n i}\psi_{\mathbf{k}\omega_n i}(\mathbf{r})$

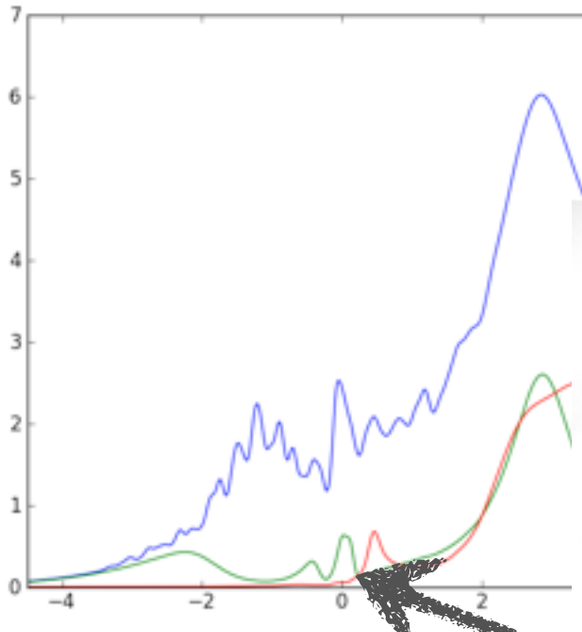
4) Determines chemical potential: $N_{val} = T\sum_{\omega_n, i} \frac{1}{i\omega_n + \mu - \varepsilon_{\mathbf{k}\omega_n i}}$

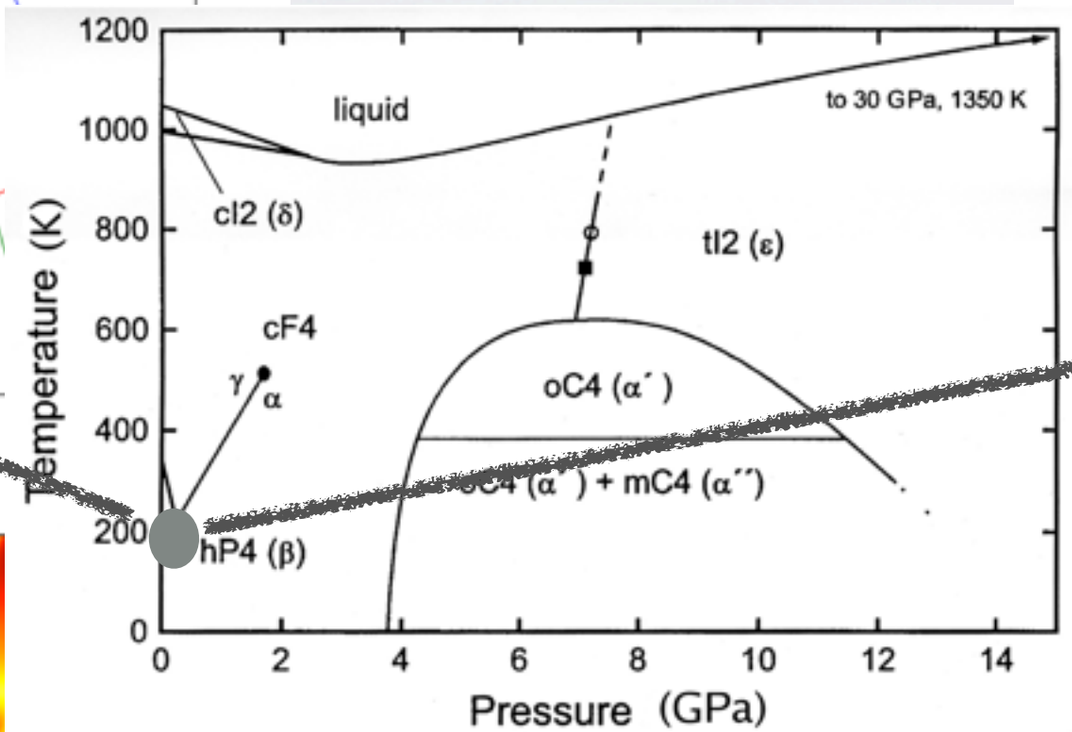
5) Calculates DMFT electronic charge in 3D space:

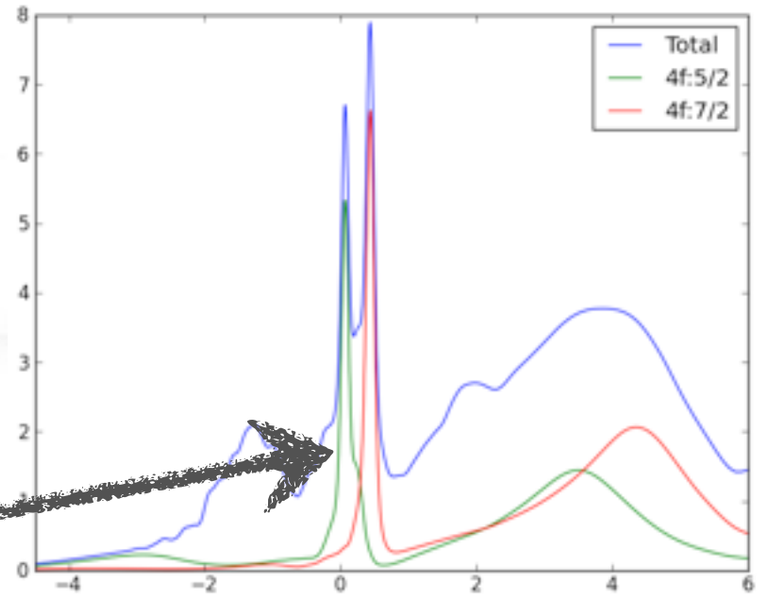
$$\rho^{DMFT}_{val} = \sum_{\mathbf{k},ij} \psi^{DFT}_{\mathbf{k}i}(\mathbf{r}) \times T\sum_{\omega_n} \left[\left(i\omega_n + \mu - \epsilon_{\mathbf{k}} - \overline{\Sigma}_{\mathbf{k}}(\omega)\right)^{-1}\right]_{ij} \times \psi^{DFT}_{\mathbf{k}j}(\mathbf{r})$$

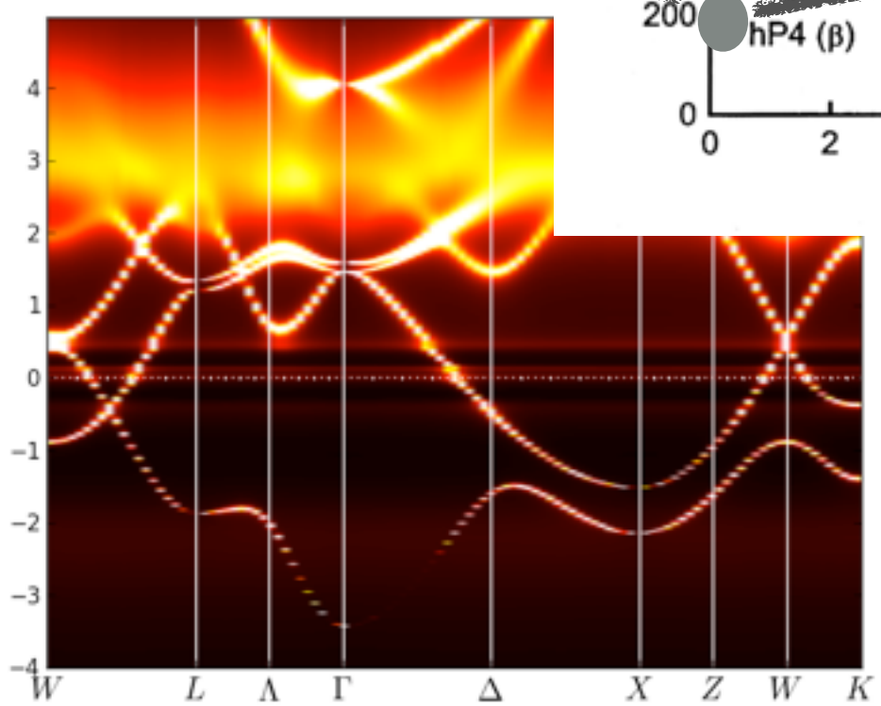
6) Calculates valence kinetic energy $E_{valence} = \mathrm{Tr}((-\nabla^2 + V_{KS})\rho^{DMFT}_{val})$

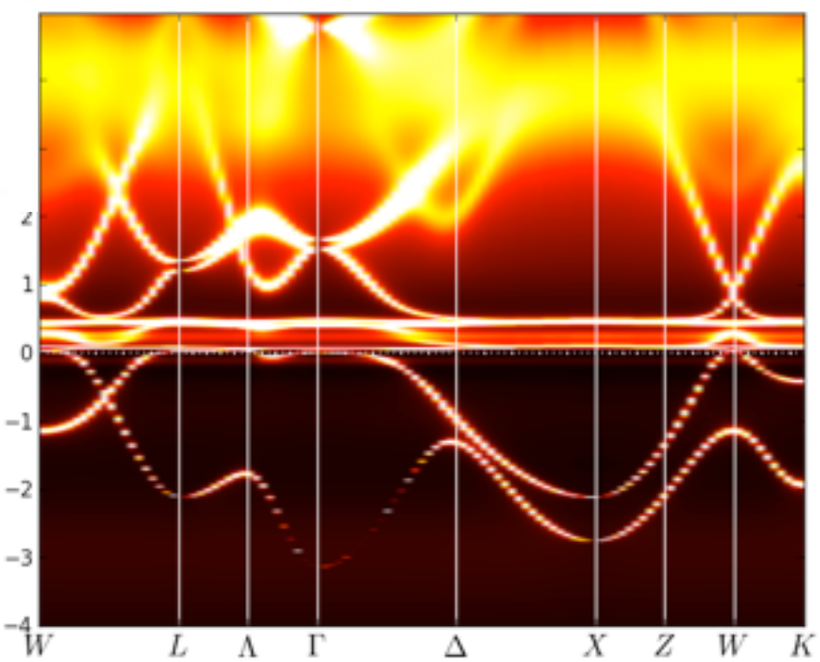
EXAMPLE 1: IsoStructural transition in Ce metal



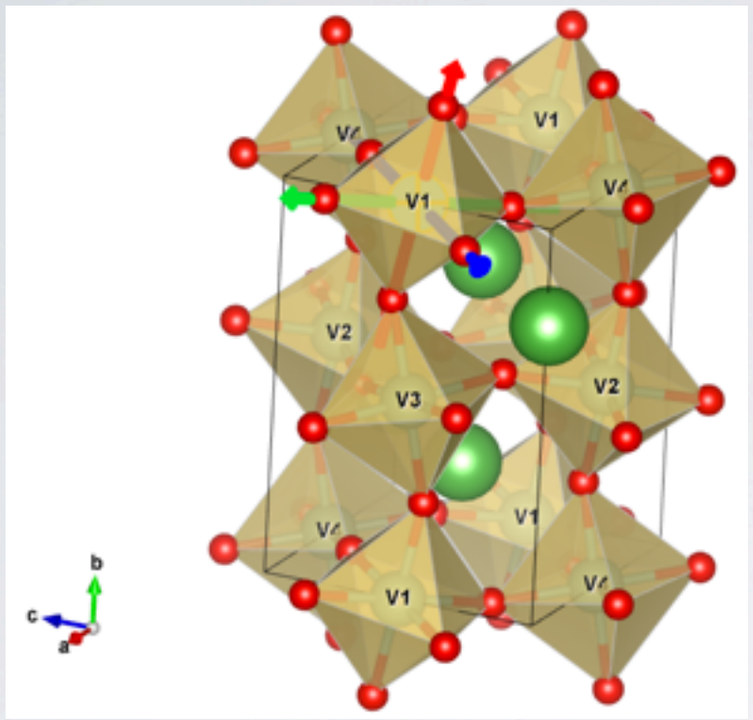


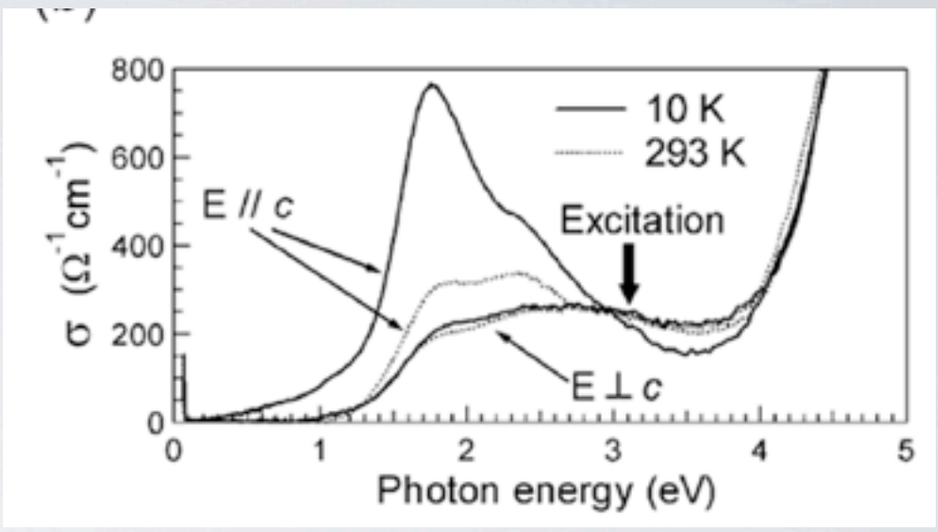






EXAMPLE2: Mott insulator LaVO3

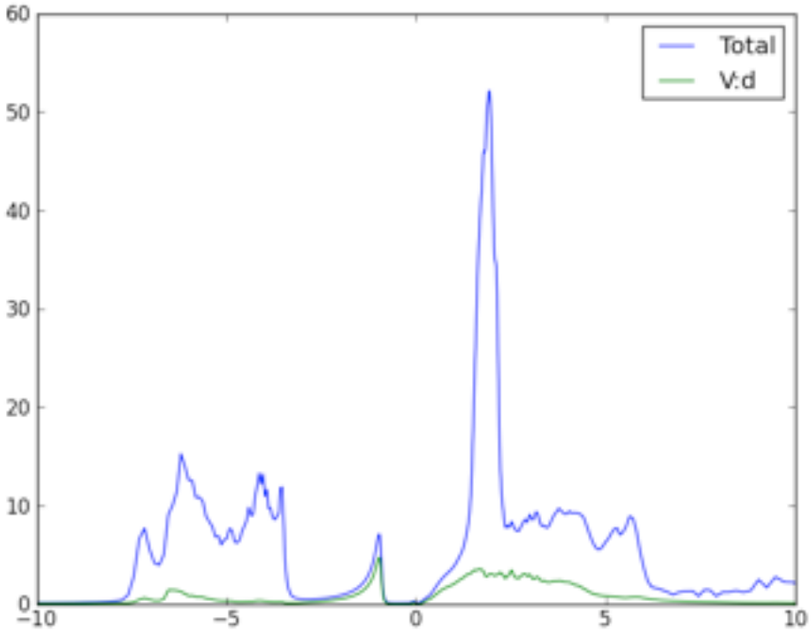


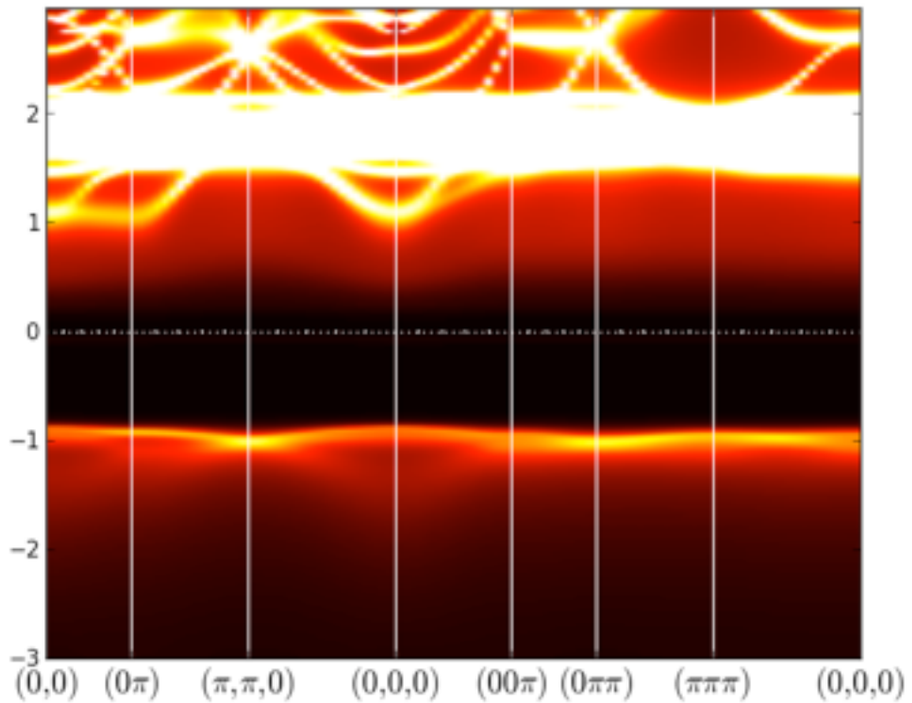


optical conductivity

Perovskite V-system with 2 electrons on V atom which localize

with a gap ~ 1.5eV





LECTURE BASED ON

Functional view on DFT+DMFT:

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

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

Implementation of DFT+DMFT:

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

Impurity solver:

Phys. Rev. B 75, 155113 (2007), KH.

arXiv:1403.7214: P. Sémon, C.-H. Yee, KH, A.-M. S. Tremblay

Screening of interaction:

Phys. Rev. B 82, 045105 (2010), A. Kutepov, KH, S.Y. Savrasov, G. Kotliar.

Some lecture notes:

http://www.physics.rutgers.edu/~haule/509/

http://www.physics.rutgers.edu/~haule/681/

THANK YOU!